# STATISTICAL THERMODYNAMICS

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*A version of Statistical Mechanics for Students of Physics and Chemistry*

BY

THE LATE

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CAMBRIDGE

AT THE UNIVERSITY PRESS

1965

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## PREFACE TO SECOND IMPRESSION

Advantage has been taken of the reprinting to correct typographical and other trivial errors. As the reprinting has been done by photography, no other changes in the main text were possible. However, in a few cases where further corrections or additions seemed especially desirable, supplementary sections have been provided in an appendix to which references are given in the main text.

E. A. G.

*June* 1948

## PREFACE

The Kinetic Theory of Gases, developed by Clausius, Maxwell and Boltzmann, has since those days expanded so widely and deeply that the name is now entirely inadequate, and its descendent theory may be held to cover all those properties of matter in bulk which may be referred to its atomic constitution. The theory is not concerned with the properties of individual atomic systems—that is a matter for Quantum Theory—but with all properties displayed by large collections of such systems interacting with one another, so long as these properties are recognizably dependent upon the properties of the individual systems or their laws of interaction. One may hope that the ultimate content of the Descendent of the Kinetic Theory of Gases will be the whole field of the properties of matter in bulk—treated of course from the atomic standpoint and derived from atomic properties and the atomic constitution of matter. But as yet this field is not co-extensive with the properties of matter in bulk; it is more restricted and may be conveniently described as the field of the *atomic properties* of matter. Examples of properties which still fall outside the field are properties of fluid motion in gases or liquids, and the elastic and plastic properties of solids. Some such distinction will doubtless remain a permanent feature of theories of the properties of matter, for even when possible it will surely not always be convenient to treat all properties as atomic. It is unnecessary to attempt any more precise definition of these two fields; in practice no difficulty ever arises in distinguishing between them.

The old Kinetic Theory of Gases has thus developed into *The Atomic Theory of the Properties of Matter in Bulk*. In so doing it has bifurcated into (i) *The Theory of the Properties of Matter in Equilibrium*, and (ii) *The Theory of Transport Phenomena*, including theories of other rates of change such as Chemical Kinetics. The former branch is commonly referred to, perhaps rather inaccurately, as Statistical Mechanics. This branch has proved the easier in which to progress. Its field is coterminous with that of Thermodynamics, and its theorems have something of the same generality, being true no matter by what mechanism the equilibrium state in question may be reached or preserved. It is with this branch that we shall be mainly concerned in this book. Since the explicit introduction of the atomic structure of matter into Thermodynamics by this theory often leads to the direct and precise evaluation of thermodynamic functions, including various constants of integration undeterminable in classical

thermodynamics, and to a clearer understanding of the content of thermodynamic theorems, we have called the book *Statistical Thermodynamics*. The title covers adequately its contents except for the chapter on Chemical Kinetics. This subject belongs properly to a treatise on the second branch, but it does not lie conformably on an exposition of the theory of Transport Phenomena in Gases, which is the only other section of the second branch as yet well developed. Since moreover at this preliminary stage the application of equilibrium properties to further the study of chemical kinetics is peculiarly simple and direct, and since this subject is of particular interest to many students of Physical Chemistry, whose needs we have particularly in mind, it seems proper to include some account of it here.

The title Statistical Thermodynamics could almost as well have been applied to the monograph *Statistical Mechanics* (the theory of the properties of matter in equilibrium) by one of us, of which a second (enlarged) edition has recently been published. But it appeared to us that there were cogent reasons for preparing the present version of the theory in a form more suitable for the type of student whom we have in mind. *Statistical Mechanics* contains considerable sections of purely astrophysical interest, and many passages devoted entirely to mathematical details of the proofs of the required theorems. Moreover, on many occasions it deliberately avoids the use of ordinary thermodynamic methods. For many students of Physics and Chemistry all these features are far from advantageous. We have therefore tried to present here a modified version of Statistical Mechanics, in which the theory is developed, as nearly as may be, parallel to Thermodynamics, so as to be complementary to a presentation of that subject. Mathematical details of proofs are taken for granted, and the applications confined to terrestrial physics and chemistry. At the same time we have attempted to keep the book up to date by including an account of progress made during the past three years.

Our book then is so far as possible a link between pure Thermodynamics and pure Statistical Mechanics. It differs from Classical Thermodynamics in that the thermodynamic functions for the assemblies and phases with which we deal are not left unspecified, or to be derived solely from measurements, but are always constructed *a priori* by the application to particular molecular models of the fundamental theorems of Statistical Mechanics with which we start. We are thereby limited to substances or phases of not too great a complication, but within such limits benefit from the greater detail provided by such models. At the same time our book differs from most expositions of Statistical Mechanics in that once the laws of Thermodynamics have been derived, full use is made of them wherever this seems advantageous. We believe that no such extensive exposition making full

use of all available *a priori* evaluations of thermodynamic functions has yet been attempted, although their employment has become increasingly frequent and successful.

We have referred above to the generality of the fundamental theorems of statistical mechanics. These theorems lay down the rules by which the equilibrium state of an assembly and its thermodynamic functions are to be calculated. They are formulated here in Chapter I, but their truth is assumed without further analysis. Our present interest lies solely in their applications. Their truth, however, is far from obvious or elementary, and they merit profound analysis, which leads to a field of study quite distinct from the field of this book. We have been the more willing to omit all reference to any such analysis of the fundamental theorems for two reasons. In the first place, an adequate discussion requires a book of much the same size as our discussion of the applications. In the second place, just such a book, almost entirely devoted to a study of the foundations, has recently been written by Tolman (*Foundations of Statistical Mechanics*, Oxford, 1938), and the student who wishes to study this field cannot do better than turn to Tolman.

In accordance with the utilitarian nature of our book, we have tried to give sufficient references to enable the reader to find more detailed information on the subjects discussed, but we have almost entirely omitted references with regard to that part of the theory which has now become classical. In using experimental data for comparison with theory we have tried to select the most reliable and accurate data and have not included data which are now of merely historical interest.

We wish to thank all our friends and colleagues who have so freely given us the benefit of their expert knowledge. Unfortunately they are too numerous for us to mention them all, but we are particularly indebted to Dr M. Blackman, Dr R. A. Buckingham, Dr T. S. Chang, Dr H. Jones and Professor F. Simon.

It is a pleasure to acknowledge the unfailing helpfulness and efficiency of the Cambridge University Press.

For mathematical proofs or finer details we shall frequently refer the reader to *Statistical Mechanics* (Cambridge, 1936), which will be denoted by *S.M.* For derivations of classical thermodynamic formulae we shall give references to *Modern Thermodynamics by the Methods of Willard Gibbs* (Methuen, 1933), of which we have adopted the thermodynamic notation with only a few alterations; this book will be denoted by *M.T.*

R. H. F.
E. A. G.

*August* 1939

## VALUES* OF IMPORTANT PHYSICAL CONSTANTS

| | | |
|---|---|---|
| $k$ | Boltzmann's constant | $1{\cdot}380 \times 10^{-16}$ erg deg.$^{-1}$ |
| $\mathsf{N}$ | Avogadro's number | $6{\cdot}023 \times 10^{23}$ molecule mole$^{-1}$ |
| $\mathsf{N}^{-1}$ | Mass of molecule with unit molecular weight | $1{\cdot}660 \times 10^{-24}$ g. |
| $-\vert e\vert$ | Charge of electron | $4{\cdot}8025 \times 10^{-10}$ e.s.u. |
| $m_e$ | Mass of electron | $9{\cdot}107 \times 10^{-28}$ g. |
| $c$ | Speed of light | $2{\cdot}998 \times 10^{10}$ cm. sec.$^{-1}$ |
| $h$ | Planck's constant | $6{\cdot}624 \times 10^{-27}$ erg sec. |
| $\beta$ | Bohr's magneton | $9{\cdot}273 \times 10^{-21}$ erg gauss$^{-1}$ |

* Birge, *Phys. Soc. Rep. Prog. Phys.* **8**, 90 (1941).

Conversion factors of various energy units to centigrade degrees

$$k^{-1} = 7{\cdot}244 \times 10^{15} \text{ deg./erg} = 1{\cdot}4385 \text{ deg./wave number}$$
$$= 1{\cdot}1605 \times 10^{4} \text{ deg./electron volt.}$$

$$R = \mathsf{N}k = 8{\cdot}314 \times 10^{7} \text{ erg deg.}^{-1} \text{ mole.}^{-1} = 8{\cdot}314 \text{ joule deg.}^{-1} \text{ mole.}^{-1}$$
$$= 8{\cdot}205 \times 10^{-2} \text{ litre atm. deg.}^{-1} \text{ mole.}^{-1} = 1{\cdot}986 \text{ cal. deg.}^{-1} \text{ mole.}^{-1}$$

Two numerical factors frequently required

$$\mathsf{N}(h^2/2\pi mkT)^{\frac{3}{2}} = 3{\cdot}25\,(100/MT)^{\frac{3}{2}} \text{ cm.}^3$$ $m$ mass of molecule in g. $M$ chemical molecular weight.

$$h^2/8\pi^2 AkT = 39{\cdot}6/10^{40}\,AT$$ $A$ moment of inertia in g.cm.$^2$

In the table below the symbols for the chief thermodynamic functions are correlated with those used by other authors.

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| | This book | $S$ | $E$ | $F$ | $G$ | $H$ | $\mu$ |
| 1876 | Gibbs | $\eta$ | $\epsilon$ | $\psi$ | $\zeta$ | $\chi$ | $\mu$ |
| 1923 | Lewis and Randall | $S$ | $E$ | $A$ | $F$ | $H$ | F |
| 1924 | Partington | $S$ | $U$ | $F$ | $Z$ | $H$ | $\mu$ |
| 1929 | Schottky | $S$ | $U$ | $F$ | $G$ | $W$ | $\mu$ |
| 1933 | Guggenheim | $S$ | $E$ | $F$ | $G$ | $H$ | $\mu$ |
| 1936 | Fowler | $S$ | $E$ | $F$ | $G$ | $H$ | $\mu$ |
| 1936 | Bronsted | $S$ | $E$ | $F$ | $G$ | $H$ | $\mu$ |
| 1936 | Van Rysselbergh | $S$ | $E$ | $F$ | $G$ | $H$ | $\mu$ |
| 1937 | Zemansky | $S$ | $U$ | $F$ | $G$ | $H$ | $\mu$ |
| 1939 | MacDougall | $S$ | $E$ | $A$ | $F$ | $H$ | $\mu$ |
| 1939 | MacInnes | $S$ | $U$ | $F$ | $Z$ | $H$ | $\mu$ |
| 1939 | Slater | $S$ | $U$ | $A$ | $G$ | $H$ | — |
| 1940 | Mayer | $S$ | $E$ | $A$ | $F$ | $H$ | — |
| 1944 | Prigogine and Defay | $S$ | $E$ | $F$ | $G$ | $H$ | $\mu$ |
| 1946 | De Boer | $S$ | $U$ | $F$ | $G$ | $W$ | $\mu$ |
| 1948 | This book | $S$ | $E$ | $F$ | $G$ | $H$ | $\mu$ |

# CHAPTER I

## INTRODUCTION

## THE FUNDAMENTAL ASSUMPTIONS OF STATISTICAL MECHANICS

§ **100. Introduction.** The object of Statistical Mechanics, or the theory of the properties of matter in equilibrium, is to derive the properties of matter in bulk from the known or assumed atomic structure of matter and the laws of interaction between its constituent atoms. The properties of matter in bulk exhibited to our senses, even when reinforced by the most sensitive instruments, are the properties of large collections of individual atoms. The behaviour of an individual atom or molecule is never here in question, only the result of the combined behaviour of the multitude. The establishment of the properties of individual atoms and their laws of interaction is no part of the programme laid down for statistical mechanics. This is the programme of the quantum theory, and in this book all such properties and laws as are required may be assumed to be known. At the present time much indeed is known in this field, but there are still vast gaps in our knowledge, and in the absence of direct information we may and shall make any definite assumptions concerning such properties and laws as may seem reasonable and compatible with the general body of exact knowledge.

A particular homogeneous piece of matter may be a gas, a liquid, a solid, or a surface film. In the case of a gas we have to deal with a collection of more or less independent atoms or molecules which only occasionally interact sensibly with one another. In the case of a solid the atoms or molecules are very far from being nearly independent, but we can often analyse the motions of the atoms into nearly independent vibrations of the solid in its normal modes. In other cases such an analysis into nearly independent systems may be less accurate or at present practically impossible. It will then be found that progress in the application of statistical mechanics becomes increasingly difficult. In fact, progress made may in general be measured by the extent to which it has been possible to analyse the states and motions of the complex material into the states and motions of suitable almost independent systems. For this reason a convenient habit has grown up of referring to the matter under discussion as an *Assembly* of *Systems*. The systems may or may not be atoms, but whatever they are, their properties are determined by quantum theory and are assumed to be completely known. The assembly contains a large number of systems, and the deter-

mination of the observable equilibrium properties of the assembly, under given large scale conditions, is the primary object of statistical mechanics. In the most recent successful applications, the distinction between the assembly and its constituent systems is sometimes impossible or inconvenient to preserve. The assembly may then be taken to consist of a single system, but in that case the system itself is a complicated one, and possesses a very large number of possible states densely distributed in energy. The necessary treatment will be found to be unaffected. Though the description of matter as an assembly of a very large number of systems is thus inessential and not always convenient, it will tend to clarity to use it, wherever possible, and we shall do so through all the earlier chapters.

As we have already said, the behaviour of an individual system in an assembly, for example an atom of helium in a litre of helium gas at normal temperature and pressure, is never in question here. This is a fortunate fact, for the behaviour of the individual atom is impossibly complicated by the numerous interactions with the walls and the other atoms of the gas, and no matter whether we try to calculate its behaviour by the laws of quantum mechanics, or, in the simpler limiting case, by the laws of classical mechanics, we find its course equally impossible to follow. Its quantal course, it is true, is not a definite trajectory like its classical course, but this can scarcely make almost complete confusion any worse confounded. It is therefore at first sight somewhat surprising that the relevant properties of an assembly can be successfully calculated, when the individual behaviour of any one of its systems lies far beyond the power of our analysis to determine. A little reflection, however, shows one that one's surprise is unjustified and that in fact one is familiar with similar states of affairs in everyday life. For in the first place in determining the relevant *molar** properties of the assembly we are stating incomparably less about the assembly than if we could specify the complete trajectory of a single atom, a specification which would actually involve specifying the trajectories of all the atoms. In the second place, such a determination of molar properties is really (as we shall soon see) a statement of the *average* or *most probable* behaviour of a large number of systems, and significant statements about averages are familiar to us in everyday life in the practice of insurance companies. It is completely impossible to say whether a given man of thirty, now alive and in apparently good health, will or will not die within the year. But it is at the same time perfectly possible to state accurately the average number of such persons in the present population of Great Britain who will so die, or in other words, the chance of death within the year to which each individual is subject.

* By *molar* we mean the properties of the matter in bulk or of the assembly as a whole; in the example chosen, its pressure, heat capacity, and atomic distribution laws.

**§ 101. The first fundamental assumption of statistical mechanics. The atomic structure of matter.** We have probably already made it sufficiently clear that statistical mechanics starts with

*Assumption I. The atomic constitution of matter.*

To-day this hardly ranks as an assumption, but it is relevant to start by recalling that it is made, since any reference to atomic constitution is foreign to classical thermodynamics.

An atom itself is of course not a simple system, but consists of a nucleus and a set of electrons in motion about the nucleus. It is often necessary to take explicit account of the electronic structure of the atom (or the molecule) in statistical applications, though not in the simplest of these. The electrons of all atoms have identical properties and a negative charge which we denote* by $-|e|$. Each electron has also a spin with angular momentum $\frac{1}{2}(h/2\pi)$, where $h$ is Planck's constant, which may be oriented either parallel or antiparallel to any applied field. The nucleus has a charge $+Z|e|$, where $Z$ is the atomic number. The behaviour of the atom or molecule is given in detail by quantum theory and we shall assume that any properties we require have been so determined.†

The above analysis of atoms into electrons and nuclei may not always be sufficient for the needs of a statistical problem. The nucleus itself (except for hydrogen) is not a simple system, but is composed (probably) of $Z$ protons and $A-Z$ neutrons, where $A$ is the mass number, that is the nearest integer to the atomic weight of the species of atom in question on the chemical scale. In some applications of statistical mechanics it is necessary to take explicit account of the detailed structure of the nucleus, but this is seldom or never necessary in applications to terrestrial physics or chemistry. All that is commonly necessary for such problems is to remember that the structure of the nucleus may manifest itself through the nuclear *spin*. We may be required to allow for various nuclei having various possibilities of orientation. It is fortunate that we require no further detail, or else the applications of statistical mechanics to terrestrial physics and chemistry would be held up for lack of a sound theory of the more detailed structure of the nucleus, just as this lack is likely to hold up many astrophysical applications.

The comments we have just made should make it clear that the first

* There is thus no danger of confusion as to whether the symbol $e$ denotes the algebraic or the numerical charge on the electron.

† There are many excellent expositions of Quantum Theory, some of which will be familiar to most of our readers. Those who have not already read a standard work of this type may find it convenient to refer to Pauling and Wilson, *Introduction to Quantum Mechanics* (McGraw-Hill, 1935). This book contains all the quantal formulae that we shall require to use.

assumption of statistical mechanics would be more correctly described thus:

*Assumption I. Matter is composed of electrons, protons and neutrons. For ordinary purposes the protons and neutrons may be regarded as combined into a number of permanent nuclei of definite constitution, internal energy and spin.* Any assembly is therefore strictly to be regarded as an assembly of a large number of electrons, protons and neutrons, whose behaviour is controlled by the laws of quantum mechanics. In more refined discussions than any we shall attempt here, positive electrons, negative protons, quanta of radiation and possibly neutrinos may also have to be admitted. This extension of the field actually causes no formal difficulty when it is necessary.

As we have already mentioned, what we, as terrestrial physicists and chemists, require to know about such an assembly is what will be the ordinarily observable properties of the matter it represents when left to itself to come to equilibrium with its surroundings.

We know, to start with, that the assembly obeys the laws of quantum mechanics, and that, in suitable conditions frequently realized in practice, these laws may be taken to reduce to their simpler limiting form, classical mechanics. We shall assume without proof any general results of quantum or classical mechanics necessary for the discussion here, and it will be convenient now to summarize the more important of these, which form the basis for Assumption II of statistical mechanics shortly to be introduced.

**§ 102. General nature of the states of an assembly.** The assembly of electrons, protons and neutrons, or of electrons and nuclei, is a part of all matter. All other matter in the universe may naturally be idealized into fields and walls which are regarded as a more or less *conservative** field of force under whose influence the assembly has certain properties which we wish to determine. Under such conditions the equation of Schrödinger for the assembly can be set up and in principle solved. If the assembly is contained in a finite volume with suitable walls, it is known that the quantal equation of Schrödinger admits of discrete eigen values $E_0, E_1, E_2, \ldots$ of the energy, to each of which there correspond one or more distinct solutions of the equation which are called eigen functions. The eigen functions themselves are often not of primary importance in statistical mechanics; what is here of primary importance is the mere fact that such solutions exist, representing possible states of motion of the assembly. Such states of motion, which are of fundamental importance, are called *stationary states* or simply *states*. By a state in this sense we always mean a state of motion corre-

* By conservative we mean that the field of force is derived from a potential energy which is a function of position only and is independent of time.

sponding to some one distinct solution of Schrödinger's equation for the assembly—to each solution one state and *vice versa*. For a large assembly of ideally almost independent systems there may be a very large number of eigen functions and therefore of states corresponding to any one possible energy value of the assembly. For other large assemblies there will be in any case a large number of states corresponding to eigen values of the energy lying in the range $E$, $E+dE$. It is in any event more natural to discuss a small energy range than an exact energy, since no actual assembly is really subject to exactly conservative fields of force, but is continually losing and gaining small amounts of energy to its surroundings by atomic encounters, even in an equilibrium state.

We therefore consider our assembly with a given energy or range of energies, to which there corresponds a large number of possible states, and have next to ask how such an assembly will behave according to the laws of quantum mechanics.

If Schrödinger's equation which we have set up to describe the complete assembly were exact, and if it included exactly every interaction between the systems of the assembly and every interaction with walls and outside bodies, then in principle we could suppose it to be exactly solved and every eigen value and eigen function would then belong to a true stationary state in which the assembly (genuinely isolated) could persist for an indefinite time. The properties of the assembly would then be the properties of this single stationary state. Such a state of affairs however is never actually realizable even to the roughest approximation. In the first place we have neglected radiation and radiative processes in the formulation of Schrödinger's equation, and have assumed that all the interactions of the assembly with the external world can be represented by conservative forces. It is in principle impossible to represent the possible interactions with radiation by any time-independent conservative fields of force; nor can the action of the actual walls and external systems be represented by time-independent terms in the potential energy. The result of this is that it is impossible for a strictly conservative Schrödinger's equation to be set up, and the exact solutions, apparently possible in principle, are actually in practice illusory. The most that is possible even in principle is to set up and solve exactly an approximate Schrödinger's equation, which must be regarded in principle as subject to time-dependent disturbances, technically known as perturbations, inevitably causing transitions from one would-be stationary state to another. Thus it is in principle never the properties of a single (true) stationary state that concern us, but some sort of average over, or selection from, a large number of stationary states, all perhaps of the same energy or distributed over a small energy range.

Now that we have been forced to admit the principle that it will never be possible for any assembly, with which we are concerned, to be regarded as existing permanently in a true stationary state, no matter how assiduously we set up and solve Schrödinger's equation, we may frankly admit that in practice Schrödinger's equation could never be set up and solved to the required accuracy. When in practice we actually set up and solve Schrödinger's equation for an assembly, we could never aim at such refinements. We rather aim to set up an equation of sufficient accuracy which can actually be sufficiently accurately solved. Its eigen values and stationary states are necessarily only approximate, and transitions between the stationary states are necessarily present, due to all the neglected interactions, which now include for convenience some interactions (more or less weak or infrequent) between the systems of the assembly itself. But the state can be nearly stationary, the eigen values good approximations to the best possible for the assembly; the properties of the assembly can be sought for by averaging in the correct manner over the properties of the right selection of these approximate stationary states.

We are now confronted with the following situation. We have set up and solved the approximate Schrödinger's equation for the assembly, the errors in this equation being represented by perturbation terms, which continually induce transitions amongst the group of stationary states for the approximate Schrödinger's equation, lying in a more or less strictly defined energy range. We may regard such a formulation as exact in principle, since there is nothing in principle to prevent an ideally exact formulation being made of the perturbation terms. For time-dependent terms are now admissible, while they were not admissible in an exact equation which was to possess perfect stationary states for its eigen functions. Such an assembly left in unaltering surroundings may theoretically be expected to present certain features, invariable to our senses and instruments, which we may call its observable equilibrium properties. Since in fact assemblies always do present such invariable features, we shall if necessary make use of this fact, in default of rigorous proof, that such properties of the assembly must exist and are determinable. It only remains to determine from our assumed knowledge of the properties of the individual stationary states of the assembly what its actual observable properties must be.

Here we meet the essential difficulty, for we have to find out how to select the correct stationary states, whose properties will dominate and determine the observable properties of the assembly. We have to decide whether the assembly, when left to itself in the way already specified, tends to settle down mainly into one or other of a small preferred group of stationary states, whose properties are or control the equilibrium properties

of the assembly; or whether it shows no such discrimination, but wanders apparently or effectively at random over the whole range of stationary states made accessible by the general conditions of the problem. In the latter case the equilibrium properties of the assembly can only be those of the vast majority of stationary states, and we can only hope to calculate equilibrium properties by taking a suitable average over all stationary states, or by selecting the properties of the most abundant or most probably occupied type of stationary state, or by some other such device, for the use of which we shall require justification.

**§ 103. The second fundamental hypothesis of statistical mechanics. The rule for averaging.** The choice of states, which must be made for the purpose defined in the preceding section, cannot yet be based on completely rigorous *a priori* reasons. It can be made in a variety of ways all of which lead fortunately to identical physical results when applied to large assemblies. We shall not describe these varieties of choice here, nor the background of theory which makes them plausible, but shall formulate at once that version of the necessary fundamental hypothesis, which we shall adopt in the rest of this book.* The ultimate justification for any version of the fundamental hypothesis is its unbroken success in application. We adopt therefore here from among several alternatives the following:

*Assumption II. Enumerate all the distinct states of the assembly consistent with a specified energy or energy range and any other given general conditions. The value $\bar{Q}$ of any property $Q$ of the assembly, which will be found to characterize the equilibrium state of the assembly, subject to the specified conditions, may be obtained by averaging over all these states, attaching to each state an equal weight (unity). Formally*

$$\bar{Q} = \Sigma_{\text{states}}\, Q/\Sigma_{\text{states}}\, 1. \qquad (103, 1)$$

This statement is still somewhat vague and must be further refined.†

We have already selected states of given energy for the averaging process. This seems perfectly natural, even without further analysis, because the assemblies that we contemplate are supposed to have constant or approximately constant energies, so that in such a condition the properties of states of other energies can hardly be expected to be relevant. But one may well question whether there are not other functions of the atomic variables of the assembly equally important, whose constancy may form part of the other general conditions mentioned in the enunciation of Assumption II.

* One may the more readily omit any discussion of the theoretical foundation of the fundamental hypothesis since it has recently been elaborately re-examined by Tolman, *The Principles of Statistical Mechanics* (Oxford, 1938). No short or simple discussion is of any great value.

† This enunciation is repeated in a refined form in § 107.

A search for such functions will put us in the way of understanding the general concept of *accessibility*, which must be introduced before a sharply defined form of Assumption II can be given.

**§ 104. A description of a classical assembly.** We have hitherto avoided all reliance on classical mechanics, and almost all reference to it, since we know nowadays that classical mechanics is in principle inapplicable to atomic assemblies, and gives correct results only in suitable limiting cases. But it will be convenient at this stage to describe a classical assembly and study conditions of accessibility in classical mechanics, since this forms a natural introduction to the somewhat more subtle conditions of accessibility imposed by the quantum theory.

An assembly obeying the laws of classical mechanics is fully described when its energy is given as a function of $N'$ generalized coordinates and the $N'$ generalized momenta corresponding to them. If the external fields of force to which the assembly is subject are conservative, the energy of the assembly may be written in Hamilton's form $H(x, p_x)$, where $x$ is short for the $N'$ coordinates $x_1, x_2, \ldots, x_{N'}$, and $p_x$ for the corresponding momenta $p_{x_1}, p_{x_2}, \ldots, p_{x_{N'}}$. In this case* no other variables enter $H$. For the idealised assembly in a conservative field of force the classical Hamiltonian equations of motion are

$$\frac{dx}{dt} = \frac{\partial H}{\partial p_x}, \quad \frac{dp_x}{dt} = -\frac{\partial H}{\partial x}, \qquad (104, 1)$$

$2N'$ equations in all. The coordinates $x$ may be any suitable set, which must just suffice to describe the geometrical configuration of the assembly at any moment. For example, for a set of $N$ structureless particles each of mass $m$, a natural set of coordinates would be the $3N$ cartesian coordinates

$$x_\alpha, y_\alpha, z_\alpha \quad (\alpha = 1, 2, \ldots, N)$$

of the $N$ particles. The corresponding (technically *conjugate*) momenta are then the $3N$ variables

$$m\dot{x}_\alpha, m\dot{y}_\alpha, m\dot{z}_\alpha \quad (\alpha = 1, 2, \ldots, N).$$

From equations (1) one can deduce that

$$\frac{dH}{dt} = 0, \qquad (104, 2)$$

which tells us that the energy does not vary with time. We can write (2) in the integrated form

$$H(x, p_x) = E, \qquad (104, 3)$$

* If the assembly is not in a conservative field of force, for example, if the walls and other bodies external to the assembly are defined by coordinates, other than the $x$'s in $H$, which are themselves functions of the time ,this time-dependent part can be abstracted from $H$ and introduced later on as a perturbation. These time-dependent forces we shall for the moment neglect, remembering, however, that in principle they can never be absent from any actual assembly.

where $E$ is a constant. Any such relationship, in which a definite one-valued function of all or any of the $2N$ variables $x$, $p_x$ is constant throughout the motion of the assembly, is called a *uniform integral* of the equations of motion. Thus formula (2) tells us that the energy is a uniform integral of the equations of motion.

The complete behaviour of a classical assembly is known when all the coordinates $x$ and momenta $p_x$ are known as functions of the time. This suggests a geometrical representation of the (classical) state of the assembly which is found helpful in any general discussion. The state of the assembly at any instant being fully known when all the $x$'s and $p_x$'s are known, we represent the state of the assembly by a point in hyper-space of $2N'$ ($=6N$) dimensions, the $x$'s and $p_x$'s being cartesian coordinates of the point. This space is known as *the phase space of the assembly*, and the path traced out by the point in phase space as its *trajectory*. This trajectory obeys the equations of motion (1) of the assembly, and for a conservative assembly is fully defined by these equations and its starting point. Two trajectories of a definite conservative assembly can never intersect. Any trajectory is moreover confined to the hyper-surface in phase space determined by (3). When non-conservative perturbations are acting, corresponding extra terms must be included in these equations, and the perturbed trajectory is naturally more complicated. It can best be thought of as approximating, over more or less lengthy periods, to one or other of the family of unperturbed trajectories through all points of phase space enclosed between two neighbouring energy surfaces separated by not too wide an energy interval $dE$, and making from time to time more or less gradual transitions from one trajectory of the family to another. The trajectories of the family may be so defined that they are the exact trajectories of a suitable conservative assembly, approximating to the actual perturbed assembly.

The value to us of a discussion of a classical assembly resides in the *Limiting Principle*, that the classical assembly can always be regarded as a limiting form of the corresponding quantal assembly. In order to be able to use classical theorems as an illustration of the corresponding exact quantal ones, it is necessary to know how the discrete eigen states of the quantum theory compare in distribution with the continuously variable states corresponding to points in classical phase space. Fortunately the complete answer to this question has long been known. It is that for an assembly of $N'$ degrees of freedom each distinct eigen function, satisfying the proper boundary conditions and Schrödinger's equation for the assembly, corresponds to an extension $h^{N'}$ of classical phase space. This correspondence is suggested in the first instance as a general theorem true for large quantum numbers as part of Bohr's *Correspondence Principle*, and can be checked by direct

evaluation in numerous simple cases.* For our purposes in this book it is sufficient to accept as a fact the correspondence between each quantal state and an extension $h^{N'}$ of phase space.

**§ 105. Accessibility; mainly classical.** In classical assemblies of the type just described, it is known that other uniform integrals, besides the energy, may well exist in certain circumstances. The components of linear and angular momentum of the assembly are unaffected by the interactions of the systems among themselves, and when not upset by the outside world are said to be conserved. They are then such uniform integrals. It is conceivable *a priori* that the class of uniform integrals might have yet other members. Any such uniform integral has a far-reaching effect on the trajectory of the representative point in phase space. A uniform integral is, as we have already explained, a relationship of the form

$$F(x, p_x) = \text{const.} \tag{105, 1}$$

For example, the constancy of the $x$-component of linear momentum in an assembly of simple particles of mass $m$ is expressed by the relation

$$\Sigma_r\, p_{x_r} = \text{const.}, \tag{105, 2}$$

and the constancy of the $x$-component of angular momentum by the equation

$$\Sigma_r\, (y_r p_{z_r} - z_r p_{y_r}) = \text{const.} \tag{105, 3}$$

The function $F$ in question is a one-valued (uniform) function of position in phase space. The existence of the uniform integral confines the trajectory to a particular surface in phase space, or, if a small range of the constant in question is allowed, to the region enclosed between two such neighbouring surfaces, exactly as the energy integral confines the trajectory to a single energy surface or a small range of such surfaces.

The possible existence of such additional uniform integrals besides the energy integral clearly shows the need for caution in our choice of the scope of the averaging or enunciation required by Assumption II. When such uniform integrals exist they must be explicitly recognised as part of the general conditions mentioned in the enunciation. We shall be required, when other uniform integrals exist, to average only over such regions of phase space, or in quantal language over such states of the assembly, as conform to their extra requirements. Such regions or states we call *accessible phase space* or *accessible states* (or *complexions*), and great care must be taken that all the requirements of accessibility are properly allowed for.

The possibility of the existence of the uniform integrals for the components of linear and angular momentum is commonly ignored, and rightly

* See Chapter II, §§ 202–204.

so, though the correct reason is not immediately obvious. Any terrestrial assembly is usually thought of as enclosed in an envelope, of more or less ideal properties, which is not itself part of the assembly. The envelope is usually idealized to the degree that it is represented by perfectly reflecting walls with which the systems of the assembly exchange no energy. It is a small step to idealize further and assume that the reflection is specular, like that of light from a mirror. The components of linear momentum are not then conserved by the assembly, as the component of any system normal to the wall is reversed when the system rebounds from the wall, and the equations of motion of the assembly admit no integral of any component of linear momentum. If the ideal envelope is spherical internally, components of angular momentum about the centre of the sphere will be unaltered by collisions with the envelope, and the components will therefore be conserved by the assembly as a whole. Actual envelopes do not have, of course, these ideal properties, and the systems exchange energy with the envelope as well as all components of linear and angular momentum, since the surface of the envelope is necessarily rough on the atomic scale. When we include the envelope in the assembly so that the uniform integrals of the energy and the momenta exist for the completed assembly, we shall find that the condition for the balance of the energy exchanges between the envelope and other parts of the assembly is equality of temperature, out of which arises the whole of thermodynamics. The conditions for the balance of the momentum exchanges however turns out to be the trivial one that the different parts of the assembly must form a unit moving like a rigid body. These conditions introduce nothing essentially new, since we may always ignore the mass motion of any part of an assembly, and consider only its internal properties relative to the motion of its centre of mass, which are unaffected by the mass motion. It makes no difference therefore in any thermodynamic discussion whether we consider that the uniform integrals of linear and angular momentum exist or not. If we wish to regard them as non-existent we consider the assembly as contained in a fixed rough envelope, and all parts of the assembly must then be at rest relative to the envelope. If we wish to regard them as existent we include the envelope in the assembly. The whole assembly must now be moving like a rigid body, and, if it is rotating, the parts of it may even be in motion relative to one another and the envelope, but their thermodynamic study is unaffected. If the systems form a gas and the envelope is rotating, the "centrifugal force" will affect the distribution of density from place to place in the gas, but the effect of this force is no different from that of the usual external force field. We shall therefore make no further reference to the uniform integrals of linear and angular momentum.

One might expect that other uniform integrals are possible for classical systems, but no others are known. One concludes that for classical assemblies the whole of phase space subject to the energy conditions is in general accessible, and therefore to be covered in the averaging process.

In drawing this conclusion, however, we have been somewhat rash, and have excluded all possibility of temporary or metastable equilibria, which are of great practical importance, and which a more careful analysis of accessibility will include in the theory. We have assumed in fact that there is *effective* free intercourse between all parts of accessible phase space during times of the order of the time of an observation or the preparation of an experiment. The qualification "effective" is essential here. It is easy to imagine conditions under which the representative point will not cover the whole of accessible phase space in such times, but that will not matter if it covers in its wanderings a representative selection of accessible phase space. It might, however, be the case that, while the representative point would cover effectively all accessible phase space *given a long enough time,* during times of the order of the time of an experiment it is effectively restricted to special regions of phase space, which alone should then be regarded as accessible, but covers these restricted regions completely. A simple example is provided by a gaseous mixture of oxygen and hydrogen at room temperature. This is in metastable equilibrium, the true equilibrium state corresponding to the almost complete conversion of the mixed gases to steam or water. The processes leading to the conversion of hydrogen molecules and oxygen molecules to water molecules are however exceedingly rare at such a temperature, and the initial numbers of oxygen and hydrogen molecules do not change during ordinary experimental times. These initial numbers are in fact effectively uniform integrals of the complete equations of motion of the assembly, and accessible phase space is effectively restricted to those regions in which these numbers retain effectively their initial values. Though the equilibrium is metastable with respect to the change consisting of the formation of water, it is otherwise perfectly normal, and all the ordinary processes of thermodynamics and statistical mechanics may be applied to evaluate its properties.

Such points are well known, but they are not always sufficiently emphasized in this connection. The important point to realize is that, even with classical assemblies, every grade of metastability is possible. In the example quoted the restrictions on the region of accessible phase space are practically perfect over long times. In other examples the restrictions may hold effectively only over limited times, and then only somewhat imperfectly. In such cases thermodynamics and statistical mechanics apply only approximately. To apply them with rigour one must always be able to lay down exact

rules of accessibility. Certain regions of phase space are completely accessible and certain other regions completely inaccessible. In practice this means that we must be able to say that corresponding statements of accessibility are effectively true for the conditions of the problem. In terms of atomic processes this means that we must be able to place all rates of change in one or other of two classes: those that are so slow that their effect can be neglected in the time of an experiment, and those that are so fast that they enable the representative point of the assembly to cover effectively the whole of phase space that they render accessible. When intermediate rates are present, thermodynamics and statistical mechanics cannot be applied. The translation of these conclusions from the language of classical phase space to that of quantum states is simple and we need not pause to undertake it.

We have emphasized these points, because their proper appreciation makes the new conditions of accessibility introduced by quantum theory appear much more natural. The finer detail of quantum mechanics has shown that not all the states of an assembly of similar systems are accessible one from another. They may be analysed into groups of non-combining states by means of their symmetry properties. The symmetry type of any suitably specified state is an absolute constant of the motion, equivalent to an exact uniform integral in classical terms. The set of accessible states for the purposes of Assumption II is the set of states (in the proper energy range) *of the correct symmetry.*

**§ 106. Accessible states for assemblies of similar systems. The symmetrical and the antisymmetrical group.** In the next chapter we shall consider in detail all possible states and accessible states for an assembly of a number of similar systems, and shall derive therefrom the important standard formulae of the equilibrium state. Here we can confine attention to general principles and determine merely how the symmetry requirements restrict accessibility.

We start with an assembly containing a set of similar systems (e.g. electrons, hydrogen molecules, helium atoms, ...). Let us consider first an assembly containing one such system whose energy in Hamilton's form is $H(x, p_x)$. For such a system Schrödinger's equation will then be

$$\left[H\left(x, -i\frac{h}{2\pi}\frac{\partial}{\partial x}\right)-\epsilon\right]\psi = 0. \tag{106, 1}$$

We use $\epsilon$ for the energy of a single system to distinguish it from the energy of the assembly which we have denoted by $E$. Possible states of the system correspond to possible solutions of this equation, for which $\psi$ satisfies the

correct boundary conditions and is bounded and one-valued in the $x$-space (*configuration space*) of the system. For an enclosed system the permissible values of $\epsilon$ can be shown to be discrete, though if the enclosure is a large one the values of $\epsilon$ may lie so close together over parts of their range that they may often be treated by a limiting process as a classical continuous distribution. These permissible values (the eigen values of the equation) will be supposed to be enumerated by a subscript taking the values 0, 1, 2, ..., so that no two values of $\epsilon$ with different subscripts are equal. Corresponding to any eigen value $\epsilon_\sigma$ of $\epsilon$ there exist one or more eigen functions $\psi_\sigma$ of equation (1). The number of such eigen functions is denoted by $\varpi_\sigma$ and is called the weight of this state. If the system is degenerate ($\varpi_\sigma \neq 1$) we can assume that it is reduced to a non-degenerate one ($\varpi_\sigma = 1$) by including suitable conservative perturbing fields, if it is convenient to do so for purposes of discussion.

Let us suppose next that our assembly is built up of two such similar systems 1 and 2 with very weak interactions, so that to a first approximation the Hamiltonian of the pair is the sum of the separate Hamiltonians. Then the complete equation of Schrödinger for the assembly is

$$\left[H\left(x_1, -i\frac{h}{2\pi}\frac{\partial}{\partial x_1}\right) + H\left(x_2, -i\frac{h}{2\pi}\frac{\partial}{\partial x_2}\right) - E\right]\Psi = 0. \qquad (106, 2)$$

It can be seen that the equation separates into two parts and that the permissible values of $E$ are $\epsilon_\sigma + \epsilon_\tau$, and the corresponding solutions

$$\Psi_{\sigma\tau} = \psi_\sigma(x_1)\,\psi_\tau(x_2), \qquad (106, 3)$$

where $\epsilon_\sigma$ and $\epsilon_\tau$ are eigen values of $\epsilon$ in (1) and $\psi_\sigma$, $\psi_\tau$ corresponding eigen functions. It is of the utmost importance to observe that in the limit of vanishing interaction the pair of systems is essentially degenerate except when $\sigma = \tau$ even if the single systems are not degenerate. For if $\sigma \neq \tau$, at least two eigen functions, $\Psi_{\sigma\tau} = \psi_\sigma(x_1)\,\psi_\tau(x_2)$, $\Psi_{\tau\sigma} = \psi_\sigma(x_2)\,\psi_\tau(x_1)$, obtained by permuting the individual systems, correspond to the same eigen value $E = \epsilon_\sigma + \epsilon_\tau$. If the single systems are degenerate ($\varpi_\sigma, \varpi_\tau \neq 1$), then the total number of distinct eigen functions corresponding to $E = \epsilon_\sigma + \epsilon_\tau$ is

$$2\varpi_\sigma\varpi_\tau \quad (\sigma \neq \tau), \text{ or } \quad \varpi_\sigma^2 \quad (\sigma = \tau).$$

The argument is quite general. If the assembly consists of $N$ weakly interacting systems, the complete equation of Schrödinger for the assembly is

$$\left[H\left(x_1, -i\frac{h}{2\pi}\frac{\partial}{\partial x_1}\right) + H\left(x_2, -i\frac{h}{2\pi}\frac{\partial}{\partial x_2}\right) + \ldots + H\left(x_N, -i\frac{h}{2\pi}\frac{\partial}{\partial x_N}\right) - E\right]\Psi = 0. \qquad (106, 4)$$

To the eigen value

$$E = \epsilon_\sigma + \epsilon_\tau + \ldots + \epsilon_\omega, \qquad (106, 5)$$

no pair of the subscripts $\sigma, \tau, \ldots, \omega$ being equal, there corresponds a set of $N!$ eigen functions obtained by permuting the systems $1, 2, \ldots, N$ among the subscripts of the eigen values $\sigma, \tau, \ldots, \omega$. A simple eigen function is

$$\Psi_1 = \psi_\sigma(x_1)\,\psi_\tau(x_2)\ldots\psi_\omega(x_N). \tag{106, 6}$$

For degenerate systems the total number of eigen functions corresponding to the eigen value (5) is

$$N!\,\varpi_\sigma\varpi_\tau\ldots\varpi_\omega. \tag{106, 7}$$

If finally we consider the completely general eigen value

$$E = n_\sigma\epsilon_\sigma + n_\tau\epsilon_\tau + \ldots + n_\omega\epsilon_\omega, \tag{106, 8}$$

where the individual eigen values are equal in groups of $n_\sigma, n_\tau, \ldots, n_\omega$, so that

$$n_\sigma + n_\tau + \ldots + n_\omega = N, \tag{106, 9}$$

then there are sets of

$$\frac{N!}{n_\sigma!\,n_\tau!\ldots n_\omega!} \tag{106, 10}$$

distinct eigen functions obtainable by permutation, of which

$$\Psi_1 = \psi_\sigma(x_1)\ldots\psi_\sigma(x_{n_\sigma})\,\psi_\tau(x_{n_\sigma+1})\ldots\psi_\tau(x_{n_\sigma+n_\tau})\ldots\psi_\omega(x_N) \tag{106, 11}$$

is typical. The total number of distinct eigen functions in the degenerate case is

$$\frac{N!\,\varpi_\sigma^{n_\sigma}\varpi_\tau^{n_\tau}\ldots\varpi_\omega^{n_\omega}}{n_\sigma!\,n_\tau!\ldots n_\omega!}. \tag{106, 12}$$

More detailed explanation of these enumerations will be found in § 205.

Any linear combinations of these eigen functions are equally eigen functions for the same value of $E$, and an equal number of any such independent linear combinations may be used in place of those so far constructed.

If to the assembly thus constructed we add another set of similar systems distinct from the set hitherto considered, we obtain a new set of eigen functions similar to (11), each of which can be combined by multiplication with each one of (11) to give an independent eigen function of the complete assembly. We may not of course permute a pair of distinguishable systems, for we do not so obtain a solution of Schrödinger's equation for the assembly. Thus for an assembly of two distinguishable sets $A$ and $B$ of similar systems corresponding to the eigen value

$$E = n_\sigma\epsilon_\sigma + n_\tau\epsilon_\tau + \ldots + n'_{\sigma'}\epsilon'_{\sigma'} + \ldots + n'_{\omega'}\epsilon'_{\omega'}, \tag{106, 13}$$

where the primed symbols refer to the $B$ systems, the number of complexion is

$$\frac{N_A!\,\varpi_\sigma^{n_\sigma}\ldots\varpi_\omega^{n_\omega}}{n_\sigma!\ldots n_\omega!}\,\frac{N_B!\,\varpi_{\sigma'}^{n'_{\sigma'}}\ldots\varpi_{\omega'}^{n'_{\omega'}}}{n'_{\sigma'}!\ldots n'_{\omega'}!}. \tag{106, 14}$$

The formulae (12), (14), and similar generalizations, must be used for enumerating the accessible states over which we have to average, provided

that the introduction of weak interactions between systems of the assembly or between the assembly and the outside world allows the assembly to pass from a state described by one of these eigen functions to any other. But this may not be so. It has been shown that the eigen functions (11) of a set of similar systems, after reorganization into suitable linear combinations, necessarily divide into a number of groups, $A, B, \ldots, S$, defined according to their symmetry properties. These groups contain between them all the eigen functions belonging to all the eigen values, and they possess the extremely important property that *no interaction of whatever type or strength between the systems, or between the systems and the outside world, so long as it is symmetrical in the coordinates of the similar systems, can ever change the assembly from an eigen function of one group $A$ to an eigen function of any other group $B$.* Thus if the assembly is originally represented by an eigen function of group $A$, it will for ever be confined to eigen functions of group $A$. Only these states are accessible.

From among the various non-combining groups two stand out, conspicuous for the simplicity of their properties and their mathematical form. One is the group of eigen functions which are symmetrical in *all* the systems. This group we shall call simply the symmetrical group $S$. Any eigen function of the $S$ group remains unaltered when we interchange the coordinates of any two of the component systems. The other group consists of eigen functions which are antisymmetrical in *all* the systems. This we shall call the antisymmetrical group $A$. Any eigen function of the $A$ group changes sign when we interchange the coordinates of any two of the component systems. These groups are unique in that for non-degenerate systems they alone contain at most one eigen function for any given eigen value $E = \Sigma_\sigma \epsilon_\sigma$. There is always exactly one member of the $S$ group; there is one member of the $A$ group if all the $\sigma$'s are different, that is if all the $n$'s are 0 or 1, and otherwise no member. This is easily verified if we observe that the antisymmetrical eigen function must take the form of the $N$-row determinant

$$\begin{vmatrix} \psi_\sigma(x_1) & \psi_\sigma(x_2) & \cdots & \psi_\sigma(x_N) \\ \psi_\tau(x_1) & \psi_\tau(x_2) & \cdots & \psi_\tau(x_N) \\ & & & \\ \psi_\omega(x_1) & \psi_\omega(x_2) & \cdots & \psi_\omega(x_N) \end{vmatrix} \qquad (106, 15)$$

while the symmetrical eigen function is the same expression expanded with all its signs positive.

These simple enumerations for assemblies of non-degenerate systems can be generalized directly to degenerate ones. For example, if $\varpi_\sigma > 1$ the other $\varpi$'s being unity as before, there are $\varpi_\sigma$ alternative $\psi_\sigma$'s which may be used in

constructing $\Psi$. It may be shown that there are therefore

$$\frac{\varpi_\sigma!}{n_\sigma!(\varpi_\sigma - n_\sigma)!} \tag{106, 16}$$

eigen functions in the $A$ group if $n_\sigma \leqslant \varpi_\sigma$, and otherwise none. In the $S$ group it may be shown that there are

$$\frac{(\varpi_\sigma + n_\sigma - 1)!}{n_\sigma!(\varpi_\sigma - 1)!} \tag{106, 17}$$

eigen functions for all values of $n_\sigma$. It is however unnecessary to establish or use these general formulae, as it is easier to pass from non-degenerate systems to degenerate ones at a later stage; we shall therefore confine attention at first to non-degenerate systems.

**§ 107. Symmetry type of the eigen functions for actual assemblies.** We know as yet no *a priori* reason why eigen functions of only one group, or of one group rather than another, should be found in nature for assemblies of particular systems. To determine the appropriate group we must still appeal to observation, and the appropriate group will vary from system to system. All material assemblies may, we believe, be correctly analysed into assemblies of electrons, protons and neutrons, at least for the ordinary purposes of thermodynamics. For these systems it is certain that the appropriate group in each case is the *antisymmetrical*. For electrons this follows from the fact that the laws of interaction of electrons must embody Pauli's exclusion principle, which is fundamental to the interpretation of spectra. According to this principle we know that two electrons in any atom may never possess the same four quantum numbers, or as we should now say, may never have the same eigen function (including spin). The group $A$ is the only group of assembly eigen functions which possesses just this property, that it has no member whenever two systems have the same system eigen function. Since the eigen functions for the collection of electrons in any atom belong to group $A$, one must suppose that this is due to the nature of the electron, and that the eigen functions for the electrons in every assembly belong to group $A$. For protons the evidence is less extensive but equally conclusive, depending on the interpretation of the hydrogen band spectrum, and the theory of the rotational heat capacity of hydrogen at low temperatures. For neutrons the evidence is less direct but still adequate, being derived mainly from a study of the properties of the deuteron, and the rotational heat capacity of deuterium. We shall assume these symmetry requirements throughout this book; the statistical evidence in support of

them will be found in its natural place among the applications described later.

Since all assemblies, as we have said, can be analysed into sets of electrons, protons and neutrons, we therefore enumerate correctly all those distinct states whose eigen functions are antisymmetrical in the electrons, protons and neutrons separately. Each such state will be called a *complexion*. So far as is known there are no further absolute restrictions to be imposed on accessibility, and in view of the successes of statistical mechanics it is unlikely that any have been overlooked. We may however in special problems at any moment encounter partial restrictions, which for suitable time scales function as absolute ones. The metastable equilibrium of a gaseous mixture of oxygen and hydrogen is one such example already mentioned. We shall meet with others in the study of heat capacities of ordinary gases such as oxygen and nitrogen, where each vibrational state exchanges vibrational energy so slowly with the kinetic energy of translation and rotation, that in the rapid adiabatic compressions in a sound wave each vibrational state functions as if its vibrational energy were a constant of the motion, and therefore as if the molecules of given vibrational quantum number were a distinct gaseous component in a gaseous mixture. We meet with yet another example, and one of the most striking, in the study of the properties of hydrogen at low temperatures, where, owing to the very small forces available for making the exchange, molecules with zero resultant nuclear spin and those with unit spin interchange only slowly, and for ordinary experiments the gas behaves as a mixture of two distinct gases with different rotational heat capacities, unless the interchange is suitably catalysed.

We have now thoroughly surveyed the field of general conditions that may or may not limit the accessibility of one quantum state (or region of phase space) from another. This is a convenient moment to summarize the investigation by re-enunciating our adopted version of Assumption II in its final form, the most precise available.

*Assumption II.* (*Adopted version of the fundamental hypothesis.*) *Enumerate all the distinct accessible states or complexions of the given assembly, each characterized by one linearly independent eigen function, consistent with a specified energy or energy range, taking account if necessary of the time scale allowed for the establishment of equilibrium. The value* $\bar{Q}$ *of any property* $Q$ *of the assembly, which will be found to characterize the equilibrium state of the assembly subject to the specified conditions, may be obtained by averaging over all these accessible states, attaching to each state an equal weight (unity). Formally*

$$\bar{Q} = \Sigma_{\text{acc. states}}\, Q / \Sigma_{\text{acc. states}}\, 1. \qquad (107, 1)$$

**§ 108. Short cuts for enumerating accessible states for ordinary assemblies.** The symmetry requirements which we have already laid down are in theory sufficient to enable us to enumerate correctly the accessible states for any assembly. But it is inconvenient, and gives little physical insight into the nature of an assembly, to regard it as a collection of so many electrons, protons and neutrons when it is actually an assembly, say, of helium atoms or hydrogen molecules themselves systems of almost perfect permanence. It seems wiser to use these units themselves as quasi-fundamental systems with secondary derived symmetry rules.

Suppose such a complex system contains $l$ electrons, $p$ protons and $n$ neutrons. Then, since interchange of a pair of complex systems means interchange of $l+p+n$ pairs of electrons, protons and neutrons, in each of which pairs the eigen function of the assembly is antisymmetrical, *the eigen function of the assembly will be symmetrical in the complex systems if* $l+p+n$ *is even, and antisymmetrical if* $l+p+n$ *is odd.* This necessary derived symmetry rule has also been proved rigorously to be sufficient.*

We are therefore able to avoid the difficulty, or rather inelegancy, mentioned above. When we have decided *a priori* from our knowledge of the properties of the secondary systems—nuclei, atoms, molecules, crystals—what systems can be properly regarded as the permanent population of the assembly in any particular problem, then we can appeal to the following

*Theorem. It is sufficient in enumerating complexions (accessible states), or rather the eigen functions of the assembly representing them, to construct formally and so to enumerate all those linearly independent eigen functions which have the correct symmetry properties in the "permanent" systems (regarded as wholes) of which the assembly is composed. The eigen functions of any "permanent" system must have the correct symmetry properties in the electrons, protons and neutrons of which that system is composed, but the direct analysis of the complete assembly into electrons, protons and neutrons may be omitted, for the number of complexions is not thereby affected.*

In conformity with this principle it is possible in most statistical problems to treat atomic nuclei as permanent complexes. No matter what the correct analysis of nuclei into more fundamental particles may be, we may always proceed by satisfying the symmetry requirements of the assembly merely in all sets of equivalent nuclei and in the extra-nuclear electrons. The symmetry rule for nuclei which holds universally, so far as is known at present, is that *the eigen functions must be antisymmetrical in all similar nuclei when the nuclei have an odd mass number and symmetrical when the*

* Ehrenfest and Oppenheimer, *Phys. Rev.* **37**, 333 (1931).

*mass number is even.* The mass number is equal to the number of protons and neutrons in the nucleus.

We have so far formulated the theorem for the analysis of "permanent" complex systems into electrons, protons and neutrons, but there is no need so to restrict it. It applies equally to the analysis of "permanent" complex systems into any "permanent" secondary systems. For example in an assembly of chlorine atoms $^{35}Cl$ the assembly eigen functions must be antisymmetrical in the $^{35}Cl$ nuclei. But the assembly will often consist entirely of "permanent" molecules $^{35}Cl_2$. Applying the principle therefore, we see that the symmetry requirements of the assembly will be satisfied, and that the enumeration of eigen functions will be correct, if we make the eigen function of each molecule *antisymmetrical* in its nuclei and then make the assembly eigen function *symmetrical* in the molecules.

The same principle may be extended to an assembly consisting of a crystal in equilibrium with its vapour. The crystal is merely a super-molecule, a system of which only one is present. We satisfy the symmetry requirements of the assembly by giving its eigen functions the correct symmetry in the free molecules in the vapour phase ignoring those in the crystal, provided that we correctly enumerate the states of the crystal itself regarded as a "permanent" system composed of that number of molecules which it happens to contain in any particular example.

**§ 109. The enumeration of complexions for localized systems.** The practical considerations of the preceding section are of value chiefly for gaseous assemblies, or at least for assemblies or parts of assemblies in which the similar systems have to be treated as on a precisely equal footing, using eigen functions from a common store; atoms or molecules in the same enclosure in a gas, or electrons in a single atom or in a single piece of metal are examples. The primary rules for electrons, protons or neutrons apply of course to all matter and all assemblies without exception, and in the above cases reduce to the practical secondary rules, whose application need merely be extended to the limits defined in the preceding sections. When, however, we need not regard the eigen functions to be used as all drawn from a common store, but may discriminate between them, the secondary rules can be still further simplified and limited.

These further limitations can perhaps be approached best by means of the following example. Let us consider an assembly which contains two different enclosures each containing electrons. We may suppose that the electrons can pass from one enclosure to the other, though only with some difficulty. In equilibrium the electrons will be partitioned between the two enclosures in a proportion which it is part of our business to determine.

But the enclosures may be supposed to be sufficiently distinct for a description of electronic states as belonging to either one enclosure or the other to be a good approximation. Let the states of the electrons belonging to one enclosure have the eigen functions $\psi_r$ and the corresponding energies $\epsilon_r$, and those belonging to the other enclosure $\psi'_r$ and $\epsilon'_r$. Let us suppose that the assembly contains five electrons, and consider the partition in which there are three in the first enclosure occupying the states represented by $\psi_1$, $\psi_2$, $\psi_3$ respectively, and two in the second enclosure occupying the states represented by $\psi'_1$, $\psi'_2$. There is of course just one accessible state of the assembly with this specification, with an eigen function antisymmetrical in all the electrons, namely that given by the determinant

$$\begin{vmatrix} \psi_1(x_a) & \psi_1(x_b) & \psi_1(x_c) & \psi_1(x_d) & \psi_1(x_e) \\ \psi_2(x_a) & \psi_2(x_b) & \psi_2(x_c) & \psi_2(x_d) & \psi_2(x_e) \\ \psi_3(x_a) & \psi_3(x_b) & \psi_3(x_c) & \psi_3(x_d) & \psi_3(x_e) \\ \psi'_1(x_a) & \psi'_1(x_b) & \psi'_1(x_c) & \psi'_1(x_d) & \psi'_1(x_e) \\ \psi'_2(x_a) & \psi'_2(x_b) & \psi'_2(x_c) & \psi'_2(x_d) & \psi'_2(x_e) \end{vmatrix}, \qquad (109, 1)$$

in which the subscripts $a$, $b$, $c$, $d$, $e$ of the coordinate $x$ specify the electrons. Suppose however instead of introducing this perfect antisymmetry we consider that electrons $a$, $b$, $c$ really belong to the first enclosure and electrons $d$, $e$ to the other. If then we construct an eigen function for the assembly with this limitation, in which the factor for the electrons in each enclosure is separately antisymmetrical for the electrons of that enclosure, we again get just one eigen function, namely

$$\begin{vmatrix} \psi_1(x_a) & \psi_1(x_b) & \psi_1(x_c) \\ \psi_2(x_a) & \psi_2(x_b) & \psi_2(x_c) \\ \psi_3(x_a) & \psi_3(x_b) & \psi_3(x_c) \end{vmatrix} \times \begin{vmatrix} \psi'_1(x_d) & \psi'_1(x_e) \\ \psi'_2(x_d) & \psi'_2(x_e) \end{vmatrix}, \qquad (109, 2)$$

and one, as we have seen, is the correct number. It can be proved (and indeed it is almost obvious) that this equivalence is perfectly general. If the assembly has any number of parts which may be regarded as distinct, each containing a definite number of similar systems, then we obtain a correct enumeration of the accessible states of the assembly by making its eigen functions show the correct symmetry properties for the exchanges of similar systems in each distinct part of the assembly. It is unnecessary in this enumeration to allow for any exchange of systems between the distinct parts or enclosures.

The permissible ignoration of symmetry requirements may thus be pushed still further. In certain assemblies the number of distinct parts or enclosures may be legitimately increased so far, that we reach a limit in which every

system belongs to its own distinct enclosure or location; the atoms in a crystal lattice provide an example. Each distinct part of the assembly now has its own one system, and if we apply the foregoing rule we see that we shall enumerate correctly the accessible states of the assembly, if we keep each system fixed in its own location, but impose no other symmetry requirement. Such an assembly or part of an assembly is called *an assembly of localized systems*, and if states are enumerated in the way described no further symmetry restrictions are required.

One important consequence of the lack of symmetry requirements for such assemblies is that the quantal enumeration of accessible states reduces to identity with the classical enumeration which has long been familiar. Suppose that the localized systems of such an assembly have states of energies $\epsilon_1, \epsilon_2, \ldots$, which are non-degenerate, each possessing one eigen function. The distribution laws of such an assembly should tell us how many of the systems ($N$ in all) will be found on the average in each state. For this study we shall find in Chapter II that we require to know how many accessible states of the assembly correspond to a state of affairs in which $n_1$ systems have an energy $\epsilon_1$, $n_2$ an energy $\epsilon_2$ and so on. This number is plainly the number of ways in which the $N$ systems can be parcelled out into groups containing $n_1, n_2, \ldots$ members, $n_1+n_2+\ldots+n_r$ being equal to $N$. This number is known to be

$$\frac{N!}{n_1!\,n_2!\ldots n_r!}, \qquad (109, 3)$$

which is therefore the required number of accessible states with the given energy distribution.

The physical difference between an assembly of localized systems which requires the classical number (3) of accessible states for all values of the $n$'s and an assembly of similar systems in a single enclosure which takes the quite different number restricted by symmetry requirements, may be illustrated as follows. In an enclosure containing similar systems there is no physical sense in saying that one system has such and such an energy *here* and another one *there*. *Here* and *there* (within the enclosure) have ceased to have any meaning in terms of the eigen functions which describe the states. But in assemblies of localized systems *here* and *there* still have a physical meaning. The assembly with a system in its $r$th state *here* is physically distinct from one with a system in its $r$th state *there*, and therefore counts as in a distinct state.

## CHAPTER II

### THE GENERAL THEOREMS FOR ASSEMBLIES OF PERMANENT SYSTEMS

**§ 200. Introduction.** We shall establish in this chapter all the usual theorems of statistical mechanics for assemblies of permanent systems (absence of chemical reactions and change of phase), which are in the highest possible degree independent of one another. These are the assemblies most amenable to exact treatment, about which most is known. The most natural application is to perfect gases, but the treatment is readily extended to crystals. It is, however, convenient to postpone this extension to crystals to Chapter IV.

The highest degree of independence is attained when it is sufficiently accurate to assume throughout the calculations that the energy of the assembly is the sum of the energies of the individual systems, and contains no part depending on the coordinates of more than one such system. On this assumption, universally if sometimes tacitly made, some comment is needed. Such an assembly is an ideal limit to which an actual assembly may approximate but can never attain. For it is essential to the whole idea of an assembly that it should form a connected dynamical system with a single energy integral, not a number of separate ones. If, indeed, the energy were really entirely independent of such cross terms, which represent the interactions of the systems, the systems would never interact and the assembly would not be connected. We have therefore to assume that some such interactions do occur, but, in this limiting case, so rarely that their contribution to the total energy of the assembly may be neglected. They still suffice to preserve connection and ensure that only a single energy integral exists. This is an example of the general assertion underlying the whole theory that, while there must exist mechanisms of interaction, their mere existence is sufficient, their nature being irrelevant to the laws of equilibrium.

**§ 201. The assignment of weights.** We have stated in Chapter I that, in averaging to determine the equilibrium state, we shall attach a weight unity to every distinct accessible state (*complexion*) of the assembly, each complexion being defined by an eigen function linearly independent of all others so used. This means that the average value $\bar{Q}$ of any quantity $Q$ is to be calculated by the equation

$$\bar{Q} = \Sigma_\sigma Q_\sigma / C, \tag{201, 1}$$

where $Q_\sigma$ denotes the value of $Q$ for the particular complexion $\sigma$, the summation $\Sigma_\sigma$ is over all complexions and $C$ denotes the total number of complexions, so that formally

$$C = \Sigma_\sigma 1. \tag{201, 2}$$

Formulae (1) and (2) can often be rearranged. In the first place a number $\Omega_\sigma$ of different complexions may for many purposes possess indistinguishable properties, e.g. the same value of $Q$. We can then regroup the summations of (1) and (2) so that they read

$$\bar{Q} = \Sigma_\sigma \Omega_\sigma Q_\sigma / C, \tag{201, 3}$$

$$C = \Sigma_\sigma \Omega_\sigma, \tag{201, 4}$$

where the summations are now over the groups of complexions. It will often be legitimate for conciseness of expression to speak of each of these groups of complexions, between whose properties we cannot or do not care to distinguish, as a single state of the assembly of weight $\Omega_\sigma$.

We next recall that our assemblies are always to be regarded as collections of practically independent systems, between which, to an approximation usually sufficient, there are no interactions. It may be shown to follow that Schrödinger's equation, which determines the eigen functions and energies of the states of the *assembly*, immediately separates into equations for the distinct *systems*. The eigen function $\Psi$ for the assembly can then be constructed out of products of the eigen functions $\psi$ for the systems. Now to any one value of the energy $\epsilon_r$ of an individual system there may belong a number $\varpi_r$ of distinct eigen functions for the system, between which we need not distinguish. We speak of $\varpi_r$ as the *weight of the system* in the given state. It is convenient to use the term *degenerate* to describe states for which $\varpi_r > 1$, and *non-degenerate* for $\varpi_r = 1$. If the assembly consists of $N$ such systems, and in a particular state of the assembly there are $n_0, n_1, \ldots, n_r, \ldots$ specified systems in states of weight $\varpi_0, \varpi_1, \ldots, \varpi_r, \ldots$, and *if no special limitations of accessibility arise*, then the weight $\Omega_\sigma$ of this group of complexions is given by the equation

$$\Omega_\sigma = \Pi_r \varpi_r^{n_r}. \tag{201, 5}$$

The formula (5) arises as follows: to each specified system can be assigned any one of its possible eigen functions, and this assignment is independent of the assignments of eigen functions to all the other systems. Thus in the case cited the first eigen function can be assigned in $\varpi_0$ ways, the second in $\varpi_0$ ways and therefore the first two together in $\varpi_0^2$ ways; to each of the first $n_0$ systems eigen functions can be assigned in $\varpi_0$ ways, and therefore to the group of $n_0$ in $\varpi_0^{n_0}$ ways. The second group can similarly be assigned eigen

functions in $\varpi_1^{n_1}$ ways, and so on. The argument and the result assume that the various specified systems are physically distinguishable in some way, so that the assignment of eigen functions $\psi(1)\,\psi'(2)$ is distinct from $\psi'(1)\,\psi(2)$, and both lead to distinct complexions.

The number of complexions $\Omega_\sigma$ given in (5) refers, as the proof shows, to the complexions provided by groups of distinct specified systems, when a *given set* of systems, $n_0$ in number, are in a state of weight $\varpi_0$ and so on. The number of complexions is much greater if *any* $n_0$ out of a total of $N$ systems may be chosen for this state, and so on for the groups in the other states. The number $\Omega_\sigma$ is then increased by a factor equal to the number of distinct ways in which groups of $n_0, n_1, \ldots, n_r, \ldots$ systems can be chosen from a total of $N$. This factor is

$$\frac{N!}{n_0!\,n_1!\ldots n_r!\ldots}, \tag{201, 6}$$

and now

$$\Omega_\sigma = \frac{N!\,\varpi_0^{n_0}\varpi_1^{n_1}\ldots\varpi_r^{n_r}\ldots}{n_0!\,n_1!\ldots n_r!\ldots}. \tag{201, 7}$$

We may again mention that these formulae hold only if there are no special restrictions of accessibility.

**§ 202. Weights of simple harmonic oscillators treated quantally and classically.** At the end of § 104 we formulated the limiting principle, which asserts that, for large quantum numbers, one obtains effectively the same result by assigning unit weight either to each linearly independent eigen function of a system or to each volume of classical phase space of extension $h^s$, where $s$ is the number of degrees of freedom of the systems.* This limiting principle can be deduced from the laws of quantum theory, but the general proof is not simple. We shall therefore merely illustrate its truth by considering its application to several important types of system.

Let us start by considering the simple case of an ideal linear harmonic oscillator. If its mass is $m$ and its classical frequency $\nu$, its classical energy equation is

$$\tfrac{1}{2}p_x^2/m + \tfrac{1}{2}(2\pi\nu)^2 mx^2 = \epsilon, \tag{202, 1}$$

where $x$ is the positional coordinate, $p_x$ the momentum and $\epsilon$ the energy, taken to be zero at rest in the position of minimum potential energy, namely the origin. In quantum theory the total energy is obtained from the corresponding equation of Schrödinger

$$\frac{\partial^2\psi}{\partial x^2} + \frac{8\pi^2 m}{h^2}\{\epsilon - \tfrac{1}{2}(2\pi\nu)^2 mx^2\}\,\psi = 0, \tag{202, 2}$$

* The content of this limiting principle is distinct from the much wider Correspondence Principle of Bohr which arose from it, and which was finally superseded by the precise relationships of quantum mechanics. But these developments have retained the limiting principle unimpaired.

and is known to have the form

$$\epsilon_v = (v+\tfrac{1}{2})\,h\nu, \tag{202, 3}$$

where the quantum number $v$ can have the values $0, 1, 2, \ldots$. To each $v$ corresponds just one eigen function $\psi_v$.

Now consider any possible orbit in classical phase space (two-dimensional in this case) whose equation is given by (1). This is an ellipse with semi-axes $(2m\epsilon)^{\frac{1}{2}}$ and $(2\epsilon/m)^{\frac{1}{2}}/2\pi\nu$. The area enclosed by this ellipse is

$$\pi(2m\epsilon)^{\frac{1}{2}}(2\epsilon/m)^{\frac{1}{2}}/2\pi\nu, \quad \text{or} \quad \epsilon/\nu.$$

Any such orbit is a classical possibility but quantum theory restricts the possible values of $\epsilon/\nu$ to $(v+\frac{1}{2})h$ with $v$ a positive integer or zero. The area of phase space between two consecutive orbits is $h$. It follows that for large quantum numbers $v$, when the permitted orbits are close together but still separated by areas $h$, an element of phase space of area $h$ corresponds to each quantum state. This verifies the correctness of the limiting principle for a simple harmonic oscillator.

**§ 203. Weights of the states of isotropic oscillators in more than one dimension.** A two-dimensional isotropic harmonic oscillator is suitable for the next illustration of weight counting, and of the limiting principle. Its classical energy equation is

$$\tfrac{1}{2}(p_x^2+p_y^2)/m + \tfrac{1}{2}(2\pi\nu)^2 m(x^2+y^2) = \epsilon. \tag{203, 1}$$

The corresponding equation of Schrödinger is

$$\frac{\partial^2\psi}{\partial x^2} + \frac{\partial^2\psi}{\partial y^2} + \frac{8\pi^2 m}{h^2}\{\epsilon - \tfrac{1}{2}(2\pi\nu)^2 m(x^2+y^2)\}\,\psi = 0. \tag{203, 2}$$

This equation separates in $x$ and $y$. The eigen functions are of the form

$$\psi = \psi_{v_x}(x)\,\psi_{v_y}(y), \tag{203, 3}$$

where $\psi_{v_x}(x)$ and $\psi_{v_y}(y)$ are eigen functions for a simple harmonic oscillator. The corresponding energy values are

$$\epsilon = (v_x+\tfrac{1}{2})\,h\nu + (v_y+\tfrac{1}{2})\,h\nu = (v_x+v_y+1)\,h\nu \quad (v_x=0,1,2,\ldots;\ v_y=0,1,2,\ldots). \tag{203, 4}$$

Each energy value is specified by a distinct value of $v_x+v_y = v$, say. But each value of $v$ can be obtained by $v+1$ distinct combinations of $v_x$ and $v_y$. Thus the value of $\epsilon$ given by $\epsilon = (v+1)\,h\nu$ corresponds to $v+1$ distinct eigen functions. The energy level $\epsilon = (v+1)\,h\nu$ therefore has a weight $v+1$. To verify the limiting principle we have therefore to show that the volume of classical phase space associated with one quantal energy level has a value which for large values of $v$ is not significantly different from $(v+1)\,h^2$.

Now the classical phase space $(x, y, p_x, p_y)$ enclosed by the surface of constant energy $\epsilon$ has the volume

$$\int dx \int dy \int dp_x \int dp_y, \tag{203, 5}$$

extended over the region for which

$$\tfrac{1}{2}(2\pi\nu)^2\, m(x^2+y^2) + \tfrac{1}{2}(p_x^2+p_y^2)/m \leqslant \epsilon \tag{203, 6}$$

If we make the substitutions

$$X = (\tfrac{1}{2}m)^{\frac{1}{2}}\, 2\pi\nu x, \quad Y = (\tfrac{1}{2}m)^{\frac{1}{2}}\, 2\pi\nu y, \quad Z = (2m)^{-\frac{1}{2}}\, p_x, \quad W = (2m)^{-\frac{1}{2}}\, p_y, \tag{203, 7}$$

the integral (5) becomes

$$\frac{2m}{\frac{1}{2}m(2\pi\nu)^2}\int dX \int dY \int dZ \int dW, \tag{203, 8}$$

the integration now extending over the interior of the four-dimensional hypersphere

$$X^2+Y^2+Z^2+W^2 = \epsilon \tag{203, 9}$$

of radius $\epsilon^{\frac{1}{2}}$. The volume of a four-dimensional hypersphere of radius $R$ can be shown* to be $\frac{1}{2}\pi^2R^4$. Evaluation of the integral in (8) thus leads to

$$\frac{2m}{\frac{1}{2}m(2\pi\nu)^2}\,\tfrac{1}{2}\pi^2\epsilon^2 = \frac{\epsilon^2}{2\nu^2}. \tag{203, 10}$$

The extension of phase space enclosed between the surfaces $\epsilon = (v+\frac{3}{2})\, h\nu$ and $\epsilon = (v+\frac{1}{2})\, h\nu$, which is the region most naturally associated with the quantum states of energy $\epsilon = (v+1)\, h\nu$, is therefore

$$\tfrac{1}{2}h^2\{(v+\tfrac{3}{2})^2-(v+\tfrac{1}{2})^2\} = h^2(v+1), \tag{203, 11}$$

in agreement with the limiting principle.

In the same way, for a three-dimensional isotropic oscillator, the number of distinct eigen functions, which correspond to the energy value

$$\epsilon = (v+\tfrac{3}{2})\, h\nu,$$

is equal to the number of ways in which positive integral or zero values can be assigned to $v_x$, $v_y$, $v_z$ so that $v_x+v_y+v_z = v$. This number can be shown to be $\frac{1}{2}(v+1)(v+2)$. Now the classical phase space $(x, y, z, p_x, p_y, p_z)$ enclosed by the surface of constant energy $\epsilon$ can be shown to have the volume

$$\int \ldots \int dx\, dy\, dz\, dp_x\, dp_y\, dp_z, \tag{203, 12}$$

the integration extending over the region for which

$$\tfrac{1}{2}(2\pi\nu)^2\,(x^2+y^2+z^2) + \frac{1}{2m}\,(p_x^2+p_y^2+p_z^2) \leqslant \epsilon. \tag{203, 13}$$

* Such integrals are known to mathematicians as Dirichlet integrals. See for example Whittaker and Watson, *Modern Analysis*, p. 258, Ed. 4 (Cambridge, 1935).

By making substitutions similar to those of (7), it can be verified that the integral (12) is equal to

$$\left\{\frac{2m}{\frac{1}{2}m(2\pi\nu)^2}\right\}^{\frac{3}{2}} I, \tag{203, 14}$$

where $I$ denotes the volume of a six-dimensional hypersphere of radius $\epsilon^{\frac{1}{2}}$. This can be shown to be $\pi^3\epsilon^3/3!$, so that the required volume of phase space becomes

$$\left\{\frac{2m}{\frac{1}{2}m(2\pi\nu)^2}\right\}^{\frac{3}{2}} \frac{\pi^3\epsilon^3}{6} = \frac{\epsilon^3}{6\nu^3}. \tag{203, 15}$$

The extension of phase space between the surfaces

$$\epsilon = (v+2)h\nu \quad \text{and} \quad \epsilon = (v+1)h\nu,$$

which is the region most naturally associated with the quantum level $\epsilon = (v+\frac{3}{2})h\nu$, is therefore

$$\tfrac{1}{6}h^3\{(v+2)^3-(v+1)^3\} = h^3\,\tfrac{1}{2}(v^2+3v+\tfrac{7}{3}), \tag{203, 16}$$

which for large $v$ does not differ significantly from $h^3\,\frac{1}{2}(v+1)(v+2)$, in agreement with the limiting principle.

**§ 204. Weights of the states of a rigid solid of revolution without axial spin (diatomic molecule).** Another example is the rigid rotator with an axis of symmetry but no spin about that axis, which has important applications to gaseous diatomic molecules. The motion of the centre of mass separates and can therefore be ignored here.

Let $A$ be the transverse moment of inertia of the molecule, and $\theta$, $\phi$ the usual spherical polar coordinates of its axis. Then the conjugate momenta $p_\theta$, $p_\phi$ are given by

$$p_\theta = A\dot{\theta}, \quad p_\phi = A\sin^2\theta\,.\,\dot{\phi}, \tag{204, 1}$$

and the classical energy equation is

$$\frac{1}{2A}\left(p_\theta^2 + \frac{1}{\sin^2\theta}p_\phi^2\right) = \epsilon. \tag{204, 2}$$

The corresponding equation of Schrödinger is

$$\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\psi}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2\psi}{\partial\phi^2} + \frac{8\pi^2 A}{h^2}\epsilon\psi = 0. \tag{204, 3}$$

The possible values of the energy are

$$\frac{h^2}{8\pi^2 A}j(j+1) \quad (j=0,1,2,\ldots), \tag{204, 4}$$

and the corresponding eigen functions are the $2j+1$ spherical harmonics* of order $j$. The weight of the $j$th state is thus $2j+1$. The extension of phase

* See, for example, Lamb, *Hydrodynamics*, Chap. v (Cambridge, 1924).

space enclosed by the surface of constant energy $\epsilon$ is given by

$$\int_0^\pi d\theta \int_0^{2\pi} d\phi \int\int dp_\theta dp_\phi, \qquad (204, 5)$$

subject to

$$\frac{1}{2A}\left(p_\theta^2 + \frac{p_\phi^2}{\sin^2\theta}\right) \leqslant \epsilon. \qquad (204, 6)$$

The integration over $p_\theta$, $p_\phi$ gives the area of an ellipse of semi-axes $(2A\epsilon)^{\frac{1}{2}}$ and $(2A\epsilon)^{\frac{1}{2}} \sin\theta$; this area is $2\pi A\epsilon \sin\theta$. Hence the integral (5) reduces to

$$2\pi A\epsilon \int_0^\pi \sin\theta d\theta \int_0^{2\pi} d\phi = 8\pi^2 A\epsilon. \qquad (204, 7)$$

The extension of phase space between the surfaces

$$\epsilon = (j+\tfrac{1}{2})(j+\tfrac{3}{2})h^2/8\pi^2 A \quad \text{and} \quad \epsilon = (j-\tfrac{1}{2})(j+\tfrac{1}{2})h^2/8\pi^2 A,$$

which is the region most naturally associated with the quantum states of energy $\epsilon = j(j+1)h^2/8\pi^2 A$, is thus

$$h^2\{(j+\tfrac{1}{2})(j+\tfrac{3}{2}) - (j-\tfrac{1}{2})(j+\tfrac{1}{2})\} = h^2(2j+1), \qquad (204, 8)$$

in agreement with the limiting principle.

**§ 205. Enumeration of accessible states (complexions).** It is necessary next to consider in greater detail how to enumerate complexions in terms of the states of the component systems of an assembly. It is here and only here that an important divergence is possible between the classical and the quantal enumerations. We recall the distinction between localized and non-localized systems defined in Chapter I. The number of accessible states (complexions) of the assembly will be different according to whether the assembly is composed of localized or non-localized systems. We shall now consider a simple example of each type of assembly in which the states of the systems are all non-degenerate.

*Type I.* Consider first an assembly containing a set of $N$ similar linear oscillators, not necessarily harmonic, which have fixed positions in the assembly. They may for example be thought of as electrons suitably bound to the atoms of a solid. Each oscillator has a similar discrete set of stationary states which may be specified by a quantum number $r$, having the possible values $0, 1, 2, \ldots$. The eigen function for electron $a$ bound to atom $\alpha$ in its $r$th quantum state may be written $\psi_r^\alpha(x_a)$, where $x_a$ is the coordinate specifying the position of electron $a$. When $n_0, n_1, \ldots, n_t$ are the numbers of oscillators in states with quantum numbers $0, 1, \ldots, t$, we have a group of states of the assembly, which may be regarded as a single state of weight

equal to the number of distinct states in the group. As we saw in (201, 6) we can construct

$$\frac{N!}{n_0!\,n_1!\ldots n_l!} \tag{205, 1}$$

distinct eigen functions, of the type

$$\psi_0^\alpha(x_a)\ldots\psi_0^\kappa(x_k)\,\psi_1^\lambda(x_l)\ldots\psi_1^\sigma(x_s)\ldots\psi_l^\upsilon(x_u), \tag{205, 2}$$

belonging to the complexion being considered and containing $n_0$ factors $\psi_0$, $n_1$ factors $\psi_1$, and so on; the total number of factors is $N$. It is assumed that we are indifferent as to where amongst the fixed oscillators those with particular degrees of excitation are situated. A distinct function of the same type is

$$\psi_0^\lambda(x_l)\ldots\psi_0^\kappa(x_k)\,\psi_1^\alpha(x_a)\ldots\psi_1^\sigma(x_s)\ldots\psi_l^\upsilon(x_u) \tag{205, 3}$$

in which just the energy levels of the electrons $a$ and $l$ have been interchanged. In all these eigen functions each electron belongs to the same atom and they are not antisymmetrical in the electrons. But by permuting the $N$ electrons among the $N$ atoms we can, as described in §§ 108, 109, make up exactly one eigen function, from each of those enumerated in (2), which is antisymmetrical in the electrons. Hence the enumeration (1) is correct though it ignores symmetry requirements and treats the electrons as permanently attached to their own atoms.

*Type II. Assembly of non-localized systems.* Consider next an assembly containing a set of $N$ electrons (or other systems all similar) free to move about in the *same* enclosure of given volume. The eigen functions now lose their distinctive superscripts $\alpha, \ldots, \kappa, \ldots$. When now $n_0, n_1, \ldots, n_l$ are again the numbers of electrons or other systems in states of given quantum number $r$, we can still make up unsymmetrical eigen functions of type (2) to the number given by (1). But now when we attempt to construct an eigen function for the assembly antisymmetrical in all the electrons, we can construct only one, if every $n$ is equal to 0 or 1, and otherwise none; and if we attempt to construct a symmetrical eigen function for another type of system, we can always construct just one, as shown in § 107.

We now have all the data required for calculating the average properties of an assembly of either type. This we now proceed to do, commencing with an assembly of localized systems.

**§ 206. An assembly of two sets of localized linear oscillators.** For simplicity of exposition we consider first this special case, which will serve to bring out all the distinctive features of the problem and the method. Let us suppose that the assembly consists of two large sets of localized linear oscillators $A$ and $B$, of total numbers $N_A$ and $N_B$. Each oscillator $A$ has a series of stationary states of weight unity, in which its energy takes the

values $\epsilon_0, \epsilon_1, \ldots, \epsilon_r, \ldots$, and each oscillator $B$ similarly has a series of stationary states of weight unity, with energy values $\eta_0, \eta_1, \ldots, \eta_s, \ldots$. We may emphasize once again that in assigning individual stationary states and energies to the systems separately we tacitly assume that they are practically independent systems, each pursuing its own motion undisturbed for the greater part of time. This is essential to the energy specification and therefore essential to the treatment of assemblies composed of large numbers of practically independent systems. At the same time we must assume that exchanges of energy between the oscillators are possible and do occasionally take place, otherwise the systems will not form a connected assembly, and obviously cannot possess unique equilibrium distribution laws. In the present very special case we may think of the exchanges of energy as effected by a few free atoms in an enclosure containing the oscillators—so few in number compared with the oscillators that we may ignore their energy altogether.

It is our object to determine the distribution laws of this assembly, that is, the equilibrium or average distribution of the oscillators among the various states which they can occupy. A specification of this distribution —equilibrium or not—may be referred to as a specification of the *statistical state of the assembly*. This conveys correctly the idea that it is only the macroscopic state of the assembly that really interests us, not the microscopic state. If, for example, forty-seven systems $A$ have the energy $\epsilon_5$, we are not interested in which of the $N_A$ systems these forty-seven may be. At the same time, since the systems are localized, a statement that such and such of the $N_A$ systems are these forty-seven is significant.

An accessible statistical state of the assembly can be specified by choosing any set of positive integers (zero included) $n_r$, $n'_s$ which satisfy the conditions

$$\Sigma_r n_r = N_A, \qquad (206, 1)$$

$$\Sigma_s n'_s = N_B, \qquad (206, 2)$$

$$\Sigma_r n_r \epsilon_r + \Sigma_s n'_s \eta_s = E, \qquad (206, 3)$$

where $E$ is the energy of the assembly. For quantal assemblies there is no temptation to use anything but an exact value of $E$ in (3), but the whole of our preliminary discussion in Chapter I referred to a small given energy range $E$, $E+dE$ rather than to an exact value. This refinement is customarily omitted and we shall justify this omission in § 207. At the moment we must admit that logically (3) should be replaced by

$$E \leqslant \Sigma_r n_r \epsilon_r + \Sigma_s n'_s \eta_s \leqslant E + dE, \qquad (206, 3)'$$

where $E$, $E+dE$ define the range in which the energy of the assembly may be assumed to lie. It will however be convenient for the sake of simplicity

to carry through the discussion first for an exact value of $E$ using (3) rather than (3)$'$.

For given $N_A$, $N_B$ and $E$ any set of positive or zero integers $n_r$, $n'_s$, chosen in this way, describes a possible statistical state of the assembly. The energies of the $A$ systems may be referred to an arbitrary zero and likewise the energies of the $B$ systems; these two arbitrary zeros of $\epsilon_r$ and of $\eta_s$ determine the zero that is to be used for $E$. The conditions (1), (2), (3) express the facts that the total number of $A$ systems is $N_A$, that the total number of $B$ systems is $N_B$, and that the total energy is $E$. Since the assembly is of type I and the system weights are all unity, the number of complexions corresponding to this statistical state is

$$\frac{N_A!}{n_0!\,n_1!\ldots n_r!\ldots}\,\frac{N_B!}{n'_0!\,n'_1!\ldots n'_s!\ldots}, \tag{206, 4}$$

by obvious extension of (201, 6). The total number $C$ of complexions is given by the equation

$$C = \Sigma_n \Sigma_{n'} \frac{N_A!}{n_0!\,n_1!\ldots n_r!\ldots}\,\frac{N_B!}{n'_0!\,n'_1!\ldots n'_s!\ldots}, \tag{206, 5}$$

summed for all $n$, $n'$ subject to (1), (2), (3).

The equilibrium distribution laws for the assembly are obtained by averaging over all complexions. We can therefore find at once an expression for the average value $\overline{n_t}$ of $n_t$, or of any similar quantity, for we have, as in (201, 3),

$$C\overline{n_t} = \Sigma_n \Sigma_{n'} \frac{n_t N_A!}{n_0!\,n_1!\ldots n_r!\ldots}\,\frac{N_B!}{n'_1!\,n'_2!\ldots n'_s!\ldots}. \tag{206, 6}$$

One of the most important average quantities is $\overline{E_A}$, the average energy of the systems $A$. This is given by

$$C\overline{E_A} = \Sigma_n \Sigma_{n'} \frac{(\Sigma_r n_r \epsilon_r)\,N_A!}{n_0!\,n_1!\ldots n_r!\ldots}\,\frac{N_B!}{n'_0!\,n'_1!\ldots n'_s!\ldots}. \tag{206, 7}$$

All such summations are of course over the values of $n$, $n'$ satisfying (1), (2), (3). We shall now show that expressions such as (5), (6) and (7) are all coefficients in certain rather simple power series. The mathematical operations, on which we shall rely, are much simplified if all the $\epsilon_r$, $\eta_s$ are integral multiples of the unit of energy without common factors. This condition can hardly ever be fulfilled exactly, but by choosing a suitably small unit of energy we can fulfil it to a high degree of approximation. We shall assume that the unit of energy has been so chosen. It can be shown that though it may be impossible to fulfil these conditions, the final result is not affected.*

* *S.M.* § 3·8.

We commence by constructing the function $f_A(z)$ defined by

$$f_A(z) = z^{\epsilon_0} + z^{\epsilon_1} + z^{\epsilon_2} + \ldots = \Sigma_r z^{\epsilon_r}, \qquad (206, 8)$$

called the *partition function* for the systems $A$, and we consider the product

$$\{f_A(z)\}^{N_A} = \{\Sigma_r z^{\epsilon_r}\}^{N_A}. \qquad (206, 9)$$

If this is expanded* by the multinomial theorem in powers of $z$, the general term is

$$\frac{N_A!}{n_0!\, n_1! \ldots n_r! \ldots} z^{\Sigma_r n_r \epsilon_r} \quad (\Sigma_r n_r = N_A). \qquad (206, 10)$$

Similarly, if we construct $f_B(z)$ defined by

$$f_B(z) = z^{\eta_0} + z^{\eta_1} + z^{\eta_2} + \ldots = \Sigma_s z^{\eta_s}, \qquad (206, 11)$$

and expand $\{f_B(z)\}^{N_B}$ in powers of $z$, the general term is

$$\frac{N_B!}{n_0'!\, n_1'! \ldots n_s'! \ldots} z^{\Sigma_s n_s' \eta_s} \quad (\Sigma_s n_s' = N_B). \qquad (206, 12)$$

By multiplying these series together it follows that the coefficient of $z^E$ in the expansion of

$$\{f_A(z)\}^{N_A} \{f_B(z)\}^{N_B} \qquad (206, 13)$$

is

$$\Sigma_n \Sigma_{n'} \frac{N_A!}{n_0!\, n_1! \ldots n_r! \ldots} \frac{N_B!}{n_0'!\, n_1'! \ldots n_s'! \ldots}, \qquad (206, 14)$$

summed for all positive (or zero) integral values of $n$, $n'$ satisfying just the conditions (1), (2) and (3). Thus $C$ is the coefficient of $z^E$ in the expansion of

$$\{f_A(z)\}^{N_A} \{f_B(z)\}^{N_B} \qquad (206, 15)$$

in powers of $z$.

A similar expression for $C\overline{E_A}$ can be similarly determined. We have just seen that

$$\{f_A(z)\}^{N_A} = \Sigma_n \frac{N_A!}{n_0!\, n_1! \ldots n_r! \ldots} z^{\Sigma_r n_r \epsilon_r}. \qquad (206, 16)$$

If we differentiate both sides with respect to $z$ and multiply by $z$ we obtain

$$z \frac{\partial}{\partial z} \{f_A(z)\}^{N_A} = \Sigma_n \frac{N_A!\,(\Sigma_r n_r \epsilon_r)}{n_0!\, n_1! \ldots n_r! \ldots} z^{\Sigma_r n_r \epsilon_r}. \qquad (206, 17)$$

On multiplying both sides by $\{f_B(z)\}^{N_B}$ we find

$$\left\{z \frac{\partial}{\partial z} [f_A(z)]^{N_A}\right\} \{f_B(z)\}^{N_B}$$

$$= \Sigma_n \Sigma_{n'} \frac{N_A!\,(\Sigma_r n_r \epsilon_r)}{n_0!\, n_1! \ldots n_r! \ldots} \frac{N_B!}{n_0'!\, n_1'! \ldots n_s'! \ldots} z^{\Sigma_r n_r \epsilon_r + \Sigma_s n_s' \eta_s}. \qquad (206, 18)$$

These summations are taken over all positive integral values of $n$ and $n'$ satisfying (1) and (2). If therefore we select from (18) the coefficient of $z^E$

* A simple generalization of the familiar binomial theorem.

we can see by referring to (7) that we obtain $C\overline{E_A}$. *Thus $C\overline{E_A}$ is the coefficient of $z^E$ in the expansion of*

$$\left\{z\frac{\partial}{\partial z}[f_A(z)]^{N_A}\right\}\{f_B(z)\}^{N_B}. \qquad (206,19)$$

We can determine a similar formula for $C\overline{n_t}$. We have

$$C\overline{n_t} = \Sigma_n \Sigma_{n'} \frac{n_t N_A!}{n_0!\,n_1!\dots n_r!\dots}\frac{N_B!}{n_0'!\,n_1'!\dots n_s'!\dots}$$

$$= N_A \Sigma_n' \Sigma_{n'} \frac{(N_A-1)!}{n_0!\,n_1!\dots n_r!\dots}\frac{N_B!}{n_0'!\,n_1'!\dots n_s'!\dots}, \qquad (206,20)$$

where $\Sigma_n' \Sigma_{n'}$ differs from $\Sigma_n \Sigma_{n'}$ in that the summation is for all positive (or zero) $n_r$, $n_s$ satisfying

$$\Sigma_r' n_r = N_A - 1, \qquad (206,21)$$

$$\Sigma_s n_s' = N_B, \qquad (206,22)$$

$$\Sigma_r' n_r \epsilon_r + \Sigma_s n_s' \eta_s = E - \epsilon_t. \qquad (206,23)$$

If now we expand the function

$$N_A\{f_A(z)\}^{N_A-1}\{f_B(z)\}^{N_B} \qquad (206,24)$$

in powers of $z$ and pick out the term in $z^{E-\epsilon_t}$, we find that its coefficient is just the expression (20), the summations being subject to (21), (22), (23). *Consequently $C\overline{n_t}$ is the coefficient of $z^E$ in the expansion of*

$$N_A z^{\epsilon_t}\{f_A(z)\}^{N_A-1}\{f_B(z)\}^{N_B}. \qquad (206,25)$$

It thus appears that the expressions for such quantities as $C$, $C\overline{E_A}$, $C\overline{n_t}$ are the coefficients in certain power series. A rapid and powerful method of evaluating these is provided by expressing them as contour integrals and evaluating the integrals by the method of steepest descents. In the next section we shall outline briefly the method of procedure without giving detailed proof. The reader interested in the mathematics will find these given in greater detail elsewhere.* The more general reader, for whom the present book is intended, will probably be more interested in the results. These are given explicitly at the beginning of § 208, and he may accept the fact that these results follow by purely mathematical computations from the formulae (15), (19) and (25). Actually the method used leads directly to formulae for average quantities such as $\overline{E_A}$, $\overline{n_t}$ without the necessity of evaluating $C$ explicitly.

**§ 207. Summarized description of the method of steepest descents.** The quantities that we require are the coefficients in certain power series. By using Cauchy's theorem† these can conveniently be expressed as com-

* See *S.M.* § 2·31. † Whittaker and Watson, *Modern Analysis*, Chaps. v, vi, Ed. 4 (Cambridge, 1935).

plex integrals taken round a contour enclosing the origin $z = 0$. Thus we find, according to (206, 15), (206, 19) and (206, 25), that

$$C = \frac{1}{2\pi i}\int_\gamma \frac{dz}{z^{E+1}}\{f_A(z)\}^{N_A}\{f_B(z)\}^{N_B}, \qquad (207, 1)$$

$$C\overline{E_A} = \frac{1}{2\pi i}\int_\gamma \frac{dz}{z^{E+1}}\left\{z\frac{\partial}{\partial z}[f_A(z)]^{N_A}\right\}\{f_B(z)\}^{N_B}, \qquad (207, 2)$$

$$C\overline{n_t} = \frac{1}{2\pi i}N_A\int_\gamma \frac{dz}{z^{E+1}}z^{\epsilon_t}\{f_A(z)\}^{N_A-1}\{f_B(z)\}^{N_B}. \qquad (207, 3)$$

The contour of integration $\gamma$ may be any contour lying within the circle of convergence of these power series (radius unity) and circulating once counter-clockwise round $z = 0$.

These integrals are exact and hold for all values of $N_A$, $N_B$ and $E$. They are, however, physically significant only when $N_A$, $N_B$ and $E$ are large, since all assemblies that we can observe contain a great number of systems. We therefore require primarily the asymptotic values of these integrals when $N_A$, $N_B$ and $E$ tend to infinity in fixed ratios. This means, physically, that we require the limiting properties of the assembly when its size tends to infinity without alteration of its *intensive* properties, that is all those properties which are independent of size or extension. The properties of the finite assembly can be shown to deviate only trivially from these limiting properties. These asymptotic values can be rigorously established, in this and in the general case, by the method of steepest descents. We shall do no more than outline the method here, referring the reader to other sources for details.*

Consider the factor multiplying $dz/z$ on the positive real axis. It tends to infinity as $z \to 0$ and as $z \to 1$; somewhere between, say at $z = \vartheta$, there is a unique *minimum*. For $\gamma$ take the circle of radius $\vartheta$ and centre the origin, that is $z = \vartheta e^{i\alpha}$. Then for values of $z$ on $\gamma$, if $N_A$, $N_B$ and $E$ are large, the modulus of this factor has a strong *maximum* at $z = \vartheta$, $\alpha = 0$. Owing also to the fact that the differential coefficient of the integrand vanishes at $\alpha = 0$, the complex terms there are trivial and the whole effective contribution to the integral comes from near this point. This remains true, when there are extra factors in the integrand such as

$$z\frac{\partial}{\partial z}\log f_A = \frac{z}{f_A(z)}\frac{\partial}{\partial z}f_A(z), \qquad (207, 4)$$

which are not raised to a high power such as $E$ or $N$, and in effect such extra factors may be taken outside the sign of integration, if in them we replace

* See *S.M.* §§ 2·31, 2·32.

$z$ by $\vartheta$. The position of the critical unique minimum of the integrand on the real axis at $z = \vartheta$ is determined as the real root, lying between 0 and 1, of the equation

$$\frac{\partial}{\partial z}\left\{\frac{[f_A(z)]^{N_A}[f_B(z)]^{N_B}}{z^E}\right\} = 0, \tag{207, 5}$$

an equation which is equivalent to

$$N_A\vartheta\frac{\partial \log f_A(\vartheta)}{\partial\vartheta} + N_B\vartheta\frac{\partial \log f_B(\vartheta)}{\partial\vartheta} = E. \tag{207, 6}$$

By comparing (1) and (2) we thus find that

$$\overline{E_A} = N_A\vartheta\frac{\partial \log f_A(\vartheta)}{\partial\vartheta}. \tag{207, 7}$$

Similarly

$$\overline{E_B} = N_B\vartheta\frac{\partial \log f_B(\vartheta)}{\partial\vartheta}. \tag{207, 8}$$

By comparing (7) and (8) with (6) we see that the essential equation

$$\overline{E_A} + \overline{E_B} = E \tag{207, 9}$$

is satisfied. These equations determine the partition of energy among the two sets of oscillators in a large assembly.

In the same way, by comparing (1) and (3) we find

$$\overline{n_t} = N_A\vartheta^{\epsilon_t}/f_A(\vartheta), \tag{207, 10}$$

which from the definition of $f_A(\vartheta)$ satisfies the essential equation

$$\Sigma_r \overline{n_r} = N_A. \tag{207, 11}$$

This seems a suitable place to resume the discussion of the effect of considering a small range of energy values and using (206, 3)′ instead of (206, 3). We shall show that the change in the resulting formulae is insignificant and may be ignored.

In (206, 15) we state that, using (206, 2), the value of $C$ is the coefficient of $z^E$ in the expansion of

$$[f_A(z)]^{N_A}[f_B(z)]^{N_B} \tag{207, 12}$$

in powers of $z$. The same arguments show that, if we use (206, 3)′, the value of $C$ is the sum of the coefficients of all powers of $z$ between $z^E$ and $z^{E+dE}$ inclusive in the same expression. Similar changes must be made in the other expressions. Thus $C\overline{E_A}$ is now the sum of the coefficients of all powers of $z$ between $z^E$ and $z^{E+dE}$ inclusive in the expansion of

$$\left\{z\frac{\partial}{\partial z}[f_A(z)]^{N_A}\right\}[f_B(z)]^{N_B}, \tag{207, 13}$$

and $C\overline{n_t}$ in that of

$$N_A z^{\epsilon_t}[f_A(z)]^{N_A-1}[f_B(z)]^{N_B}. \tag{207, 14}$$

Evaluating these new expressions as contour integrals in the manner used above, we find at once that (1), (2) and (3) are replaced by

$$C = \frac{1}{2\pi i}\int_\gamma \frac{dz}{z^{E+1}}\left\{1+\frac{1}{z}+\ldots+\frac{1}{z^{dE}}\right\}[f_A(z)]^{N_A}[f_B(z)]^{N_B}, \qquad (207, 15)$$

$$C\overline{E_A} = \frac{1}{2\pi i}\int_\gamma \frac{dz}{z^{E+1}}\left\{1+\frac{1}{z}+\ldots+\frac{1}{z^{dE}}\right\}\left\{z\frac{\partial}{\partial z}[f_A(z)]^{N_A}\right\}[f_B(z)]^{N_B}, \qquad (207, 16)$$

$$C\overline{n_t} = \frac{1}{2\pi i}N_A\int \frac{dz}{z^{E+1}}\left\{1+\frac{1}{z}+\ldots+\frac{1}{z^{dE}}\right\}z^{\epsilon_t}[f_A(z)]^{N_A-1}[f_B(z)]^{N_B}. \qquad (207, 17)$$

The only new feature is the inclusion of the extra factor

$$1+\frac{1}{z}+\ .\ .+\frac{1}{z^{dE}} = \frac{(1/z)^{dE+1}-1}{1/z-1} \qquad (207, 18)$$

in each integral.

It can now be seen that every formula which involves only the ratio of two such integrals, in particular the formulae for $\overline{E_A}$ and for $\overline{n_t}$, will be absolutely unaltered in form by the extra factor. The only change enters by formula (5) for locating the position of the minimum of the integrand on the real axis, a formula which we have seen leads to the determination of $\vartheta$ in terms of $E$. This formula is now

$$\frac{\partial}{\partial z}\left\{\frac{[f_A(z)]^{N_A}[f_B(z)]^{N_B}}{z^E}\left[1+\frac{1}{z}+\ldots+\frac{1}{z^{dE}}\right]\right\} = 0, \qquad (207, 19)$$

and (6) which follows from (5) is replaced by

$$N_A\vartheta\frac{\partial \log f_A(\vartheta)}{\partial\vartheta}+N_B\vartheta\frac{\partial \log f_B(\vartheta)}{\partial\vartheta} = E+\frac{dE+1}{1-\vartheta^{dE+1}}-\frac{1}{1-\vartheta}. \qquad (207, 20)$$

It can be shown that the extra terms for all values of $\vartheta$ between 0 and 1 lie in the range 0, $dE$. Equation (20) may therefore be discussed in the form

$$E \leqslant N_A\vartheta\frac{\partial \log f_A(\vartheta)}{\partial\vartheta}+N_B\vartheta\frac{\partial \log f_B(\vartheta)}{\partial\vartheta} \leqslant E+dE. \qquad (207, 21)$$

Now it is always presupposed that $dE \ll E$. It follows at once that the difference between (21) and (6) is insignificant.

We see then that there is no significant difference between averages based on (206, 3) and those based on (206, 3)′. It will not be necessary to refer to these wider types of averages again. All formulae established for exact energy values hold without modification for the more correct averages over a small energy range.

## § 208. Average values and temperature on the statistical scale.

We recapitulate here the results obtained in § 207 by purely mathematical operations and reasoning performed on the formulae of § 206. We shall,

however, slightly generalize the statement of these results by removing the trivial restriction that there are only two types of systems $A$ and $B$.

We consider an assembly consisting of $N_A$ systems $A$, $N_B$ systems $B$, $N_C$ systems $C$, and so on, where $N_A$, $N_B$, $N_C$, ... are all large numbers. If the systems $A$ can exist in states $0, 1, 2, \ldots$, all of unit weight and energies $\epsilon_0, \epsilon_1, \epsilon_2, \ldots$, then the average number $\overline{n_r}$ of systems $A$ in the state $r$ is given by

$$\overline{n_r} = N_A \vartheta^{\epsilon_r} / \Sigma_r \vartheta^{\epsilon_r} = N_A \vartheta^{\epsilon_r} / f_A(\vartheta) \qquad (208, 1)$$

in terms of a certain parameter $\vartheta$, of which the significance will be made clear shortly. The average number $\overline{n'_s}$ of systems $B$ in the state $s$ of energy $\eta_s$ is similarly

$$\overline{n'_s} = N_B \vartheta^{\eta_s} / \Sigma_s \vartheta^{\eta_s} = N_B \vartheta^{\eta_s} / f_B(\vartheta). \qquad (208, 2)$$

There are similar formulae for the systems of other types. According to (1) and (2), the essential formulae

$$\Sigma_r \overline{n_r} = N_A, \qquad (208, 3)$$

$$\Sigma_s \overline{n'_s} = N_B \qquad (208, 4)$$

are satisfied automatically.

The average distribution of energy among the various types of systems is the following. The average value of the energy of all the systems $A$ is given by

$$\overline{E_A} = N_A \vartheta \frac{\partial \log f_A(\vartheta)}{\partial \vartheta} = \frac{N_A \Sigma_r \epsilon_r \vartheta^{\epsilon_r}}{f_A(\vartheta)}, \qquad (208, 5)$$

which satisfies the essential equation

$$\Sigma_r \overline{n_r} \epsilon_r = \overline{E_A}. \qquad (208, 6)$$

The formulae for $\overline{E_B}$, $\overline{E_C}$, and so on are similar. Finally we have the necessary equality

$$\overline{E_A} + \overline{E_B} + \overline{E_C} + \ldots = E. \qquad (208, 7)$$

If $E$ is given, this fixes $\vartheta$. Alternatively if $\vartheta$ is given, this fixes $E$.

It remains to discuss the significance of the parameter $\vartheta$ which, while mathematical in origin, is obviously fundamental in describing the state of the assembly, and should be identifiable with some physical property of the assembly. The striking feature of $\vartheta$ is that the average properties of the systems $A$, those of $B$, those of $C$ and so on are all determined by one and the same $\vartheta$. Thus $\vartheta$ *is a parameter helping to define the state of our assembly which must have the same value for all sets of systems in the assembly.* This is precisely the property which distinguishes the temperature from other parameters,* and we are therefore forced to the conclusion that $\vartheta$ plays the role of temperature. To be sure it is not the temperature measured on the usual scale, and we shall therefore call $\vartheta$ the statistical temperature, or the

* See, for example, Born, *Physikal. Zeit.* **22**, 218, 249, 282 (1921) or Lewis and Randall, *Thermodynamics*, p. 51 (McGraw-Hill, 1923).

temperature on the statistical scale. We shall shortly derive the relation between this temperature scale $\vartheta$ and the usual thermodynamic scale $T$. We may anticipate this derivation by stating that the relation is

$$\vartheta = e^{-1/kT}, \qquad (208, 8)$$

where $T$ is the temperature on the absolute (Kelvin) scale, and $k$ is a universal constant.

**§ 209. Systems of several degrees of freedom and degenerate systems.** Up to the present we have discussed the average properties of an assembly of localized linear oscillators, but we have made no specific assumptions about the oscillators except that they have a discrete series of states specified by a quantum number, and that no two of these states have the same energy value. The formulae obtained will therefore apply to any kind of system with only one degree of freedom. Actually the most important systems with only one degree of freedom are linear oscillators. But although we assumed that the states of our systems were specified by only one quantum number, we never made any use of this assumption. Consequently our formulae remain true for systems with $p$ degrees of freedom if by the state $r$ we mean the state defined by the quantum numbers $r_1, r_2, \ldots, r_p$ and of energy $\epsilon_{r_1, r_2, \ldots, r_p}$, provided no two of these energy values are equal.

Our next step is to remove the restriction that no two energy levels are equal and so to extend our formulae to degenerate systems. Suppose that there are $\varpi_r$ states of equal energy $\epsilon_r$. We group these states together and call the group a $\varpi_r$-fold degenerate state or a state of weight $\varpi_r$. Now by a suitable small alteration of the conditions to which the systems are each subject, such as the application of external fields, technically known as a perturbation, it will generally be possible to separate these $\varpi_r$ energy levels so that the system becomes non-degenerate. We can then apply all our formulae, the partition functions $\Sigma_r \vartheta^{\epsilon_r}$ containing one term corresponding to each of the $\varpi_r$ energy levels into which the degenerate level has been split. If now we make the perturbation tend to zero, we obtain again our original system with the $\varpi_r$-fold degenerate level $\epsilon_r$. The partition function $\Sigma_r \vartheta^{\epsilon_r}$ now contains $\varpi_r$ identical terms and we therefore write it in the alternative form $\Sigma_r \varpi_r \vartheta^{\epsilon_r}$, the summation now including each degenerate state or each energy level once only.

We shall now restate our results in the form applicable to degenerate as well as non-degenerate systems. Suppose the assembly to consist of $N_A$ systems $A$, $N_B$ systems $B$ and so on. Suppose the systems $A$ have a sequence of stationary states with energies, $\epsilon_0, \epsilon_1, \ldots, \epsilon_r, \ldots$ and weights $\varpi_0, \varpi_1, \ldots, \varpi_r, \ldots$. We construct the partition function

$$f(z) = \varpi_0 z^{\epsilon_0} + \varpi_1 z^{\epsilon_1} + \ldots + \varpi_r z^{\epsilon_r} + \ldots. \qquad (209, 1)$$

The average number $\overline{n_r}$ of systems $A$ in the degenerate state of energy $\epsilon_r$ is then by extension of (208, 1)

$$\overline{n_r} = N_A \varpi_r \vartheta^{\epsilon_r}/f(\vartheta). \qquad (209, 2)$$

The energy associated with this particular group of systems $A$ is therefore by (2)

$$N_A \varpi_r \epsilon_r \vartheta^{\epsilon_r}/f(\vartheta). \qquad (209, 3)$$

The average energy $\overline{E_A}$ of all the systems $A$ is given, by summing (3) over all states $r$, in the form

$$\overline{E_A} = N_A \Sigma_r \varpi_r \epsilon_r \vartheta^{\epsilon_r}/f(\vartheta) = N_A \vartheta \frac{\partial \log f(\vartheta)}{\partial \log \vartheta}. \qquad (209, 4)$$

Exactly analogous formulae apply to the $B$ and other types of systems, the same $\vartheta$ being used throughout. Finally we have the necessary equality

$$\overline{E_A} + \overline{E_B} + \ldots = E. \qquad (209, 5)$$

If $E$ is given, this fixes $\vartheta$ the temperature on the statistical scale. Alternatively if the temperature $\vartheta$ is given, then the formulae fix $E$.

The partition function $f(\vartheta)$ is presumed to refer to the localized system. It should be observed that, in the important special case in which the motion splits up into two or more parts entirely independent of one another, the partition function $f(\vartheta)$ must factorize into functions of the same type, which refer separately to the independent motions. A particular case of this factorization occurs approximately for the rotations and vibrations of a diatomic molecule. It occurs accurately for the separation of the translatory motion from the internal motions and rotations of a free molecule, but in general free molecules are members of a gaseous phase and their complexions require an enumeration of type II.

**§ 210. Linear harmonic oscillators.** It is natural at this stage to consider a few examples of special systems and construct their partition functions.

We have already described the linear harmonic oscillator in § 202; its eigen functions $\psi_v$ are characterized by the single quantum number $v$ which can take the values

$$v = 0, 1, 2, \ldots \qquad (210, 1)$$

and the corresponding energy values are

$$\epsilon_v = (v + \tfrac{1}{2}) h\nu, \qquad (210, 2)$$

relative to an energy zero of rest at the equilibrium position. The partition function is therefore

$$f(\vartheta) = \Sigma_v \vartheta^{(v+\frac{1}{2})h\nu} = \vartheta^{\frac{1}{2}h\nu}(1 - \vartheta^{h\nu})^{-1}. \qquad (210, 3)$$

Hence in terms of the statistical temperature $\vartheta$ the average energy of $N_A$ linear harmonic oscillators will be, according to (209, 4),

$$\bar{E}_A = N_A \vartheta \frac{\partial}{\partial \vartheta} \log\{\vartheta^{\frac{1}{2}h\nu}(1-\vartheta^{h\nu})^{-1}\}$$

$$= N_A \left\{ \tfrac{1}{2}h\nu + \frac{h\nu}{\vartheta^{-h\nu}-1} \right\}. \qquad (210, 4)$$

The average energy of a single oscillator is therefore

$$\frac{\bar{E}_A}{N_A} = \tfrac{1}{2}h\nu + \frac{h\nu}{\vartheta^{-h\nu}-1}. \qquad (210, 5)$$

If we elect to take the energy zero as that of the lowest quantum state $(v=0)$, the energy values become

$$\epsilon_v = vh\nu, \qquad (210, 6)$$

and the corresponding average energy of an oscillator

$$\frac{\bar{E}_A}{N_A} = \frac{h\nu}{\vartheta^{-h\nu}-1}. \qquad (210, 7)$$

We shall refer to the energy $\frac{1}{2}h\nu$ of the lowest quantum state of a harmonic oscillator as its residual energy.*

§ 211. **Two- and three-dimensional harmonic oscillators.** It is instructive to start by considering an anisotropic two-dimensional harmonic oscillator, that is one whose natural frequencies of vibration in two directions at right angles are different. Referred to its position of minimum potential energy as origin and taking as $x$ and $y$ axes the principal axes of the oscillator, the classical energy equation becomes

$$\tfrac{1}{2}(p_x^2+p_y^2)/m + \tfrac{1}{2}(2\pi\nu_x)^2 mx^2 + \tfrac{1}{2}(2\pi\nu_y)^2 my^2 = \epsilon, \qquad (211, 1)$$

where $p_x$, $p_y$ are the momenta along the $x$, $y$ axes, $\nu_x$, $\nu_y$ are two frequencies related to the restoring force constants along the principal axes and $\epsilon$ is the energy referred to a zero of rest at the origin. The corresponding equation of Schrödinger is

$$\frac{\partial^2\psi}{\partial x^2} + \frac{\partial^2\psi}{\partial y^2} + \frac{8\pi^2 m}{h^2}\{\epsilon - \tfrac{1}{2}(2\pi\nu_x)^2 mx^2 - \tfrac{1}{2}(2\pi\nu_y)^2 my^2\}\psi = 0. \quad (211, 2)$$

This equation, like the classical equation (1), separates in $x$ and $y$. The $x$ and $y$ equations obtained have just the forms of the equations for linear harmonic oscillators of frequencies $\nu_x$, $\nu_y$ respectively. Consequently the

* This is a grammatically more satisfactory English equivalent of *nullpunktsenergie* than the commonly used "*zero point energy*".

energy levels are of the forms

$$\epsilon_{v_x,v_y} = (v_x+\tfrac{1}{2})h\nu_x + (v_y+\tfrac{1}{2})h\nu_y \quad (v_x = 0,1,2,\ldots,\, v_y = 0,1,2,\ldots). \quad (211,3)$$

The partition function is therefore

$$f(\vartheta) = \Sigma_{v_x}\Sigma_{v_y}\vartheta^{(v_x+\frac{1}{2})h\nu_x+(v_y+\frac{1}{2})h\nu_y} = \Sigma_{v_x}\vartheta^{(v_x+\frac{1}{2})h\nu_x}\Sigma_{v_y}\vartheta^{(v_y+\frac{1}{2})h\nu_y}$$

$$= \left(\frac{\vartheta^{\frac{1}{2}h\nu_x}}{1-\vartheta^{h\nu_x}}\right)\left(\frac{\vartheta^{\frac{1}{2}h\nu_y}}{1-\vartheta^{h\nu_y}}\right). \quad (211,4)$$

The average energy $\overline{E_A}$ distributed among $N_A$ such systems will be

$$\overline{E_A} = \vartheta\frac{\partial}{\partial\vartheta}\log f(\vartheta) = N_A\left\{\tfrac{1}{2}h\nu_x + \frac{h\nu_x}{\vartheta^{-h\nu_x}-1} + \tfrac{1}{2}h\nu_y + \frac{h\nu_y}{\vartheta^{-h\nu_y}-1}\right\}. \quad (211,5)$$

Let us now consider isotropic two-dimensional harmonic oscillators. We can obtain any formulae required by merely setting $\nu_x = \nu_y = \nu$ in the corresponding formula for the anisotropic oscillators. It is more usual to class together all states of equal energy, that is all states of given values of $v_x+v_y$ into degenerate states specified by $v = v_x+v_y$. By (3) the $v$th degenerate state will have an energy $(v+1)h\nu$ and a weight $v+1$, since $v_x$ can have any of the $v+1$ values $0, 1, 2, \ldots, v$. Hence the partition function is

$$f(\vartheta) = \vartheta^{h\nu} + 2\vartheta^{2h\nu} + 3\vartheta^{3h\nu} + \ldots = \left[\frac{\vartheta^{\frac{1}{2}h\nu}}{1-\vartheta^{h\nu}}\right]^2. \quad (211,6)$$

Consequently the average energy $\overline{E_A}$ distributed amongst $N_A$ such oscillators is by (209, 4)

$$\overline{E_A} = N_A\vartheta\frac{\partial}{\partial\vartheta}\log f(\vartheta) = 2N_A\left\{\tfrac{1}{2}h\nu + \frac{h\nu}{\vartheta^{-h\nu}-1}\right\}, \quad (211,7)$$

in agreement with formula (5) when $\nu_x = \nu_y = \nu$. It is just twice the value for linear oscillators.

It is scarcely necessary to go through the details for a three-dimensional oscillator; if it is anisotropic the extension from the two-dimensional case is obvious. An isotropic three-dimensional harmonic oscillator will have energy levels of the form $(v+\frac{3}{2})h\nu$, where $v$ is an integer obtained as the sum of $v_x$, $v_y$, $v_z$, each of which can take any of the integral values $0, 1, 2, \ldots$. The number of such possible distinct combinations of $v_x$, $v_y$, $v_z$ to give the same sum $v$ is $\frac{1}{2}(v+1)(v+2)$. In other words, the degenerate state with energy $(v+\frac{3}{2})h\nu$ has a weight $\frac{1}{2}(v+1)(v+2)$. The partition function is then

$$f(\vartheta) = \sum_{v=0}^{\infty}\tfrac{1}{2}(v+1)(v+2)\vartheta^{(v+\frac{3}{2})h\nu} = \{\vartheta^{\frac{1}{2}h\nu}/(1-\vartheta^{h\nu})\}^3. \quad (211,8)$$

For the average energy $\overline{E_A}$ of $N_A$ such oscillators we have by (209, 4)

$$\overline{E_A} = N_A\vartheta\frac{\partial}{\partial\vartheta}\log f(\vartheta) = 3N_A\left\{\tfrac{1}{2}h\nu + \frac{h\nu}{\vartheta^{-h\nu}-1}\right\}, \quad (211,9)$$

which is just three times the value for linear oscillators, as we should expect.

**§ 212. Rigid rotators without axial spin.** The equation of Schrödinger and its solutions for these systems have already been given in § 204. We shall here describe its states from a slightly different point of view. The systems have two degrees of freedom, and therefore require two quantum numbers to define their eigen functions. Classically we can easily imagine several rotational states of equal energy, differing merely in the orientation of the axis of rotation. We might therefore expect quantally several possible states of equal energy but different orientation. This in fact occurs, and is called spatial degeneracy. If this degeneracy is removed by applying an external field, the eigen functions can be described by means of two quantum numbers $j$ and $m$ with the following physical significance. In the limit of a vanishingly small field, the total angular momentum of the system is equal to $j(j+1)h/2\pi$, while its component about an axis parallel to the field is $mh/2\pi$. The allowed values of the two quantum numbers are

$$j = 0, 1, 2, \ldots,$$
$$m = -j, -j+1, \ldots -1, 0, +1, \ldots j-1, j.$$

The energy will depend on both $j$ and $m$, but the terms depending on $m$ tend to zero as the field strength becomes vanishingly small. Thus in the limiting case of no field, the energy becomes independent of $m$, and all states of given $j$ are classed together as a degenerate state of weight $2j+1$, the number of possible values of $m$ for a given value of $j$. The energy values in the absence of an external field are

$$\epsilon_j = j(j+1)h^2/8\pi^2 A, \tag{212, 1}$$

where $A$ is the transverse moment of inertia. The partition function is therefore

$$f(\vartheta) = \sum_{j=0}^{\infty} (2j+1)\vartheta^{j(j+1)h^2/8\pi^2 A}, \tag{212, 2}$$

which cannot be further simplified without making approximations. If we make the substitution

$$\tau = \frac{h^2}{8\pi^2 A} \log \frac{1}{\vartheta}, \tag{212, 3}$$

then we have
$$f(\vartheta) = \sum_{j=0}^{\infty} (2j+1)e^{-j(j+1)\tau}. \tag{212, 4}$$

When we have correlated $\vartheta$ with temperature we shall find that in practice almost always $\tau \ll 1$. Under this condition we can obtain an approximation by replacing the sum in (4) by an integral. Using the substitution

$$j(j+1)\tau = \xi, \quad (2j+1)\tau\, dj = d\xi, \tag{212, 5}$$

we obtain

$$f(\vartheta) = \int_0^{\infty} (2j+1)e^{-j(j+1)\tau}\, dj = \frac{1}{\tau}\int_0^{\infty} e^{-\xi}\, d\xi = \frac{1}{\tau} = \frac{8\pi^2 A}{h^2 \log(1/\vartheta)}. \tag{212, 6}$$

A more exact evaluation has been obtained by Mulholland* who has shown that

$$f(\vartheta) = \frac{1}{\tau}\{1 + \tfrac{1}{3}\tau + \tfrac{1}{15}\tau^2 + O(\tau^3)\}. \tag{212, 7}$$

We shall apply this formula to diatomic molecules in Chapter III.

**§ 213. Rigid rotators with axial spin (symmetrical tops).** The states of these systems are too complicated to be discussed here and we shall merely enumerate them. If $A$ is the transverse and $C$ the axial moment of inertia the possible energy values are

$$\epsilon_{j,\lambda,m} = \frac{h^2}{8\pi^2}\left\{\frac{j(j+1)}{A} + \lambda^2\left(\frac{1}{C} - \frac{1}{A}\right)\right\}, \tag{213, 1}$$

where

$$j = 0, 1, 2, \ldots, \begin{cases} \lambda = -j, -j+1, \ldots, -1, 0, +1, \ldots, j-1, j, \\ m = -j, -j+1, \ldots, -1, 0, +1, \ldots, j-1, j. \end{cases} \tag{213, 2}$$

Since the systems have three degrees of freedom, there are three quantum numbers $j$, $\lambda$, $m$. but owing to spatial degeneracy the energy values are in fact completely determined by two of these. We may therefore omit the subscript $m$ from $\epsilon_{j,\lambda,m}$, and class together the $2j+1$ states, corresponding to different values of $m$, into a single degenerate state of weight $2j+1$. The partition function $f(\vartheta)$ may therefore be written in the form

$$f(\vartheta) = \sum_{j=0}^{\infty} \sum_{\lambda=-j}^{j} (2j+1)\, e^{-j(j+1)\tau - \lambda^2\tau'}, \tag{213, 3}$$

where

$$\tau = \frac{h^2}{8\pi^2 A}\log\frac{1}{\vartheta}, \tag{213, 4}$$

$$\tau' = \frac{h^2}{8\pi^2}\left(\frac{1}{C} - \frac{1}{A}\right)\log\frac{1}{\vartheta}. \tag{213, 5}$$

Formula (3) cannot be simplified without approximation, but in the physically important case $\tau \ll 1$, $\tau' \ll 1$ we have the approximation

$$\begin{aligned} f(\vartheta) &= \int_0^\infty (2j+1)\, e^{-j(j+1)\tau}\, dj \int_{-j}^{j} e^{-\lambda^2\tau'}\, d\lambda \\ &= \frac{2}{\tau}\int_0^\infty e^{-j(j+1)\tau - j^2\tau'}\, dj \end{aligned} \tag{213, 6}$$

by integration by parts. Since $\tau$ and $\tau'$ are small, the main contribution to this integral comes from such a long range of $j$ that $j(j+1)$ can be taken as

* Mulholland, *Proc. Camb. Phil. Soc.* **24**, 280 (1928).

$j^2$ over the greater part of the region in which the integrand is sensible. To this approximation, which is sufficient for practical applications, we have

$$f(\vartheta) = \frac{2}{\tau}\int_0^\infty e^{-j^2(\tau+\tau')}\,dj = \frac{\pi^{\frac{1}{2}}}{\tau(\tau+\tau')^{\frac{1}{2}}}$$

$$= 8\pi^2\left\{\frac{2\pi A}{h^2\log(1/\vartheta)}\right\}\left\{\frac{2\pi C}{h^2\log(1/\vartheta)}\right\}^{\frac{1}{2}}. \qquad (213,7)$$

For the completely symmetrical rotator $C = A$, and so $\tau'$ is zero. We then have a still greater degeneracy since the energy values are independent of $\lambda$ as well as of $m$. In this case

$$f(\vartheta) = \sum_{j=0}^{\infty}(2j+1)^2\,e^{-j(j+1)\tau}. \qquad (213,8)$$

In the physically important case we can again replace the sum by an integral and obtain the approximation

$$f(\vartheta) = \int_0^\infty (2j+1)^2\,e^{-j(j+1)\tau}\,dj$$

$$\sim \int_0^\infty 4j^2 e^{-j^2\tau}\,dj = \frac{\pi^{\frac{1}{2}}}{\tau^{\frac{3}{2}}}$$

$$= 8\pi^2\left\{\frac{2\pi A}{h^2\log(1/\vartheta)}\right\}^{\frac{3}{2}}. \qquad (213,9)$$

§ 214. **An assembly of two sets of non-localized systems.** We shall now develop methods for calculating the equilibrium state of an assembly, when the complexions must be enumerated in the manner detailed in § 205 for assemblies of type II. For simplicity we shall consider an assembly containing systems of two types $A$ and $B$, $N_A$ and $N_B$ in number, all of whose states are at first non-degenerate, with energy values $\epsilon_0, \epsilon_1, \ldots, \epsilon_r, \ldots$ and $\eta_0, \eta_1, \ldots, \eta_s, \ldots$ for $A$ and $B$ respectively, all expressible as integers in terms of a suitable unit of energy. The number of systems in the states with these energies will be specified as usual by $n_0, n_1, \ldots, n_r, \ldots$ and $n_0', n_1', \ldots, n_s', \ldots$. This set of numbers completely specifies a statistical state of the assembly. We have now to distinguish between two important cases, according as the eigen functions of the assembly are symmetrical or antisymmetrical in all the systems of a given set.

(i) *The assembly eigen functions are symmetrical in all the systems of a given set. Assemblies of such systems are said to obey the Bose-Einstein statistics.*

There is now one eigen function for every set of positive (or zero) integral values of the $n_r$, $n_s'$. The total number of complexions $C$ is therefore simply

equal to the number of sets of positive (or zero) integral values of the $n_r$, $n'_s$ satisfying the necessary equalities

$$\Sigma_r n_r = N_A, \qquad (214, 1)$$

$$\Sigma_s n'_s = N_B, \qquad (214, 2)$$

$$\Sigma_r n_r \epsilon_r + \Sigma_s n'_s \eta_s = E. \qquad (214, 3)$$

We shall now show that this number $C$ is equal to the coefficient of $x^{N_A} y^{N_B} z^E$ in the expansion as a power series of $x$, $y$, $z$ of the double continued product

$$\Pi_r (1 + xz^{\epsilon_r} + x^2 z^{2\epsilon_r} + \ldots)\, \Pi_s (1 + yz^{\eta_s} + y^2 z^{2\eta_s} + \ldots)$$
$$= \Pi_r (1 - xz^{\epsilon_r})^{-1}\, \Pi_s (1 - yz^{\eta_s})^{-1}. \qquad (214, 4)$$

Let us consider the factor corresponding to the $r$th state of the $A$ systems. From this we must select one term in evaluating the product which will be of the form $x^{n_r} z^{n_r \epsilon_r}$. A specimen term in the expansion of the product $\Pi_r(\;)$ is therefore $x^{\Sigma_r n_r} z^{\Sigma_r n_r \epsilon_r}$, where the $n_r$ can have any integral values (positive or zero) independently. A specimen term in the other factor $\Pi_s(\;)$ is similarly $y^{\Sigma_s n'_s} z^{\Sigma_s n'_s \eta_s}$, with similar values of the $n'_s$. The general term in the expansion of the complete expression is therefore $x^{\Sigma_r n_r} y^{\Sigma_s n'_s} z^{\Sigma_r n_r \epsilon_r + \Sigma_s n'_s \eta_s}$, in which all $n_r$ and $n'_s$ take all positive integral values (or zero) independently. If therefore from this expression we select the terms in $x^{N_A} y^{N_B} z^E$, we restrict the $n_r$, $n'_s$ to just those values which satisfy (1), (2) and (3); this coefficient is therefore $C$.

It will be observed that the $x$ and $y$ play parts similar to that played by the variable $z$. The variable $x$ selects those terms which obey the restriction of the complexions to the correct value of $N_A$, the variable $y$ selects from these terms those which obey the further restrictions to the correct value of $N_B$. Previously for localized systems these conditions were automatically fulfilled. The variable $z$ as before selects those terms which are restricted to the correct value $E$ of the energy.

Now in (4) the term $Cx^{N_A} y^{N_B} z^E$, in which we are interested, results as the sum of $C$ equal terms $x^{N_A} y^{N_B} z^E$ each corresponding to one particular complexion. Consider a particular one of these complexions and let the number of $A$ systems with energy $\epsilon_t$ in this particular complexion be $n_t$. Then the term $x^{N_A} y^{N_B} z^E$ contributed by this particular complexion will contain the factor $x^{n_t} z^{n_t \epsilon_t}$, and no other factor in which the subscript $t$ occurs. Suppose now we replace this factor $x^{n_t} z^{n_t \epsilon_t}$ by $n_t x^{n_t} z^{n_t \epsilon_t}$, and perform the same operation on the $t$ factor due to each complexion. The result will be to change the coefficient of $x^{N_A} y^{N_B} z^E$ from $\Sigma 1$ to $\Sigma n_t$, where the summation is over the $C$ complexions. According to (201, 1) this means that we change the coefficient of $x^{N_A} y^{N_B} z^E$ from $C$ to $C\overline{n_t}$ We therefore consider the expansion of

$$xz^{\epsilon_t}(1 - xz^{\epsilon_t})^{-2}\, \Pi_{r \neq t} (1 - xz^{\epsilon_r})^{-1}\, \Pi_s (1 - yz^{\eta_s})^{-1}, \qquad (214, 5)$$

obtained from (4) by replacing the $t$ factor $\Sigma_{n_t} x^{n_t} z^{n_t \epsilon_t}$ by $\Sigma_{n_t} n_t x^{n_t} z^{n_t \epsilon_t}$, or in other words replacing every term $x^{n_t} z^{n_t \epsilon_t}$ by $n_t x^{n_t} z^{n_t \epsilon_t}$. It follows that $C\overline{n_t}$ is just the coefficient of $x^{N_A} y^{N_B} z^E$ in the expansion of (5) or alternatively of

$$xz^{\epsilon_t}(1 - xz^{\epsilon_t})^{-1} \Pi_r (1 - xz^{\epsilon_r})^{-1} \Pi_s (1 - yz^{\eta_s})^{-1}. \tag{214, 6}$$

(ii) *The assembly eigen functions are antisymmetrical in all the systems of a given set. Assemblies of such systems are said to obey Fermi-Dirac statistics.*

For such an assembly there is again one eigen function for each set of allowed values of $n_r$, $n'_s$, but these allowed values are restricted to 0 and 1, values greater than 1 being prohibited in agreement with Pauli's exclusion principle. The total number of complexions $C$ is therefore equal to the number of sets of values of the $n_r$, $n'_s$ satisfying the necessary equalities (1), (2), and (3) and subject to the further restriction that each $n_r$, $n'_s$ must be 0 or 1 but may not exceed 1. This number $C$ may be shown to be equal to the coefficient of $x^{N_A} y^{N_B} z^E$ in the expansion of the double continued product

$$\Pi_r (1 + xz^{\epsilon_r}) \Pi_s (1 + yz^{\eta_s}). \tag{214, 7}$$

The proof follows the same lines as for the Bose-Einstein statistics. Again, exactly as in the Bose-Einstein statistics, we obtain $C\overline{n_t}$ as the coefficient of $x^{N_A} y^{N_B} z^E$ in an expression obtained from (7) by replacing any $t$ term $x^{n_t} z^{n_t \epsilon_t}$ by $n_t x^{n_t} z^{n_t \epsilon_t}$. In the present case the $t$ factor in (7) is $1 + xz^{\epsilon_t}$ and this has to be replaced by $xz^{\epsilon_t}$. This is equivalent to multiplying by

$$(xz^{\epsilon_t})(1 + xz^{\epsilon_t})^{-1}.$$

We see then that $C\overline{n_t}$ is equal to the coefficient of $x^{N_A} y^{N_B} z^E$ in the expansion of

$$xz^{\epsilon_t}(1 + xz^{\epsilon_t})^{-1} \Pi_r (1 + xz^{\epsilon_r}) \Pi_s (1 + yz^{\eta_s}). \tag{214, 8}$$

We observe that formulae (4) and (6) for the Bose-Einstein statistics differ only in signs from formulae (7) and (8) for the Fermi-Dirac statistics. We can therefore combine the two under a common form, and at the same time allow for the eventuality that the two sets of systems may obey different statistics. We have then the general proposition that the number of complexions $C$ is equal to the coefficient of $x^{N_A} y^{N_B} z^E$ in the expansion of

$$\Pi_r (1 \pm xz^{\epsilon_r})^{\pm 1} \Pi_s (1 \pm yz^{\eta_s})^{\pm 1}, \tag{214, 9}$$

where in the first product we use either both the + or both the − signs according as the $A$ systems obey the Fermi-Dirac or the Bose-Einstein statistics, and similarly in the second product according to the nature of the $B$ systems. Further, the average number of systems $A$ in the state $t$ is equal to the coefficient of $x^{N_A} y^{N_B} z^E$ in the expansion of

$$xz^{\epsilon_t}(1 \pm xz^{\epsilon_t})^{-1} \Pi_r (1 \pm xz^{\epsilon_r})^{\pm 1} \Pi_s (1 \pm yz^{\eta_s})^{\pm 1}. \tag{214, 10}$$

Our next step is the purely mathematical one of evaluating these coefficients, and so obtaining the value of $\overline{n_t}$ and other such average properties of the assembly. We shall briefly outline the method of procedure in the next paragraph. The reader, who is not particularly interested in the mathematics, can proceed to § 216 where the results are collected. He may accept these results as deducible from the formulae of the present section by purely mathematical reasoning.

**§ 215. Mathematical derivation.** We know that $C$ is the coefficient of $x^{N_A} y^{N_B} z^E$ in the expression (214, 9). Using Cauchy's theorem three times over as for one variable, we find

$$C = \frac{1}{(2\pi i)^3} \iiint \frac{dx\,dy\,dz}{x^{N_A+1} y^{N_B+1} z^{E+1}} \Pi_r (1 \pm xz^{\epsilon_r})^{\pm 1} \Pi_s (1 \pm yz^{\eta_s})^{\pm 1}. \quad (215, 1)$$

Similarly it follows from (214, 10) that

$$C\overline{n_t} = \frac{1}{(2\pi i)^3} \iiint \frac{dx\,dy\,dz}{x^{N_A+1} y^{N_B+1} z^{E+1}} \{xz^{\epsilon_t}(1 \pm xz^{\epsilon_t})^{-1}\} \Pi_r (1 \pm xz^{\epsilon_r})^{\pm 1} \Pi_s (1 \pm yz^{\eta_s})^{\pm 1}, \quad (215, 2)$$

the integrand of (2) differing from that of (1) only in the presence of the extra factor

$$\frac{xz^{\epsilon_t}}{1 \pm xz^{\epsilon_t}} = \frac{1}{(xz^{\epsilon_t})^{-1} \pm 1}. \quad (215, 3)$$

It can be proved that the factor multiplying $dx\,dy\,dz/xyz$ in (1), namely

$$\Pi_r (1 \pm xz^{\epsilon_r})^{\pm 1} \Pi_s (1 \pm yz^{\eta_s})^{\pm 1} / x^{N_A} y^{N_B} z^E, \quad (215, 4)$$

dominates the behaviour of the whole integrand both in (1) and (2), or in any similar integral with extra factors such as the $\{(xz^{\epsilon_t})^{-1} \pm 1\}^{-1}$ in (2). This dominant factor has for real values of the variables $x$, $y$, $z$ a unique *minimum* at a point $\lambda_A$, $\lambda_B$, $\vartheta$. Further the contours of integration can be chosen to pass through this point, so that on the contours the integrand has a single dominant *maximum* at this point whose neighbourhood contributes the whole effective value of the integral. Such a point is called a col. If then we substitute the values $\lambda_A$, $\lambda_B$, $\vartheta$ for $x$, $y$, $z$ in (3) or any similar extra factors, we may take this factor outside the sign of integration. We have therefore on dividing (2) by (1)

$$\overline{n_t} = \frac{\lambda_A \vartheta^{\epsilon_t}}{1 \pm \lambda_A \vartheta^{\epsilon_t}} = \frac{1}{\lambda_A^{-1} \vartheta^{-\epsilon_t} \pm 1}. \quad (215, 5)$$

According to the definitions of $\lambda_A$, $\lambda_B$, $\vartheta$ as the values of $x$, $y$, $z$ which make the dominant factor in the integrand stationary, they are determined by

the equations

$$\Sigma_r \frac{\lambda_A \vartheta^{\epsilon_r}}{1 \pm \lambda_A \vartheta^{\epsilon_r}} = N_A, \tag{215, 6}$$

$$\Sigma_s \frac{\lambda_B \vartheta^{\eta_s}}{1 \pm \lambda_B \vartheta^{\eta_s}} = N_B, \tag{215, 7}$$

$$\Sigma_r \frac{\epsilon_r \lambda_A \vartheta^{\epsilon_r}}{1 \pm \lambda_A \vartheta^{\epsilon_r}} + \Sigma_s \frac{\eta_s \lambda_B \vartheta^{\eta_s}}{1 \pm \lambda_B \vartheta^{\eta_s}} = E. \tag{215, 8}$$

We see from (5), (6), (7) and (8) that the necessary equalities

$$\Sigma_r \overline{n_r} = N_A, \tag{215, 9}$$

$$\Sigma_s \overline{n'_s} = N_B, \tag{215, 10}$$

$$\Sigma_r \overline{n_r} \epsilon_r + \Sigma_s \overline{n'_s} \eta_s = E \tag{215, 11}$$

are automatically satisfied.

§ **216. Summary of results.** We may summarize the results, whose deduction has been sketched in § 215, as follows, at the same time removing the trivial restriction to assemblies of only two types of systems. In an assembly containing $N_A$ systems of type $A$, $N_B$ of type $B$, and so on, the average number $\overline{n_r}$ of systems of type $A$, in the non-degenerate state $r$ of energy $\epsilon_r$, is given by

$$\overline{n_r} = \frac{\lambda_A \vartheta^{\epsilon_r}}{1 \pm \lambda_A \vartheta^{\epsilon_r}} = \frac{1}{\lambda_A^{-1} \vartheta^{-\epsilon_r} \pm 1}, \tag{216, 1}$$

which can also be written in the form

$$\overline{n_r} = \lambda_A \frac{\partial}{\partial \lambda_A} \log(1 \pm \lambda_A \vartheta^{\epsilon_r})^{\pm 1}, \tag{216, 2}$$

where we have to take the + or − according as the assembly eigen functions have to be antisymmetrical or symmetrical in the systems $A$. The $\lambda_A$, $\lambda_B$, ... are parameters of which there is one for each type of system $A$, $B$, ..., but the same parameter $\lambda_A$ occurs in formulae such as (1) for all the various states $r$ of the $A$ systems. The $\lambda_A$, $\lambda_B$, ... are determined by the necessary equalities such as

$$\Sigma_r \frac{\lambda_A \vartheta^{\epsilon_r}}{1 \pm \lambda_A \vartheta^{\epsilon_r}} = \Sigma_r \overline{n_r} = N_A. \tag{216, 3}$$

The average energy $\overline{E_A}$ of the $N_A$ systems $A$ is given by

$$\overline{E_A} = \Sigma_r \overline{n_r} \epsilon_r = \Sigma_r \frac{\epsilon_r \lambda_A \vartheta^{\epsilon_r}}{1 \pm \lambda_A \vartheta^{\epsilon_r}}$$

$$= \vartheta \frac{\partial}{\partial \vartheta} \Sigma_r \log(1 \pm \lambda_A \vartheta^{\epsilon_r})^{\pm 1}. \tag{216, 4}$$

Finally $\vartheta$ is a parameter with the same value not only for all states $r$ of one type of system, but for all the various types of systems $A, B, \ldots$. The necessary relation

$$E = \overline{E_A} + \overline{E_B} + \ldots \tag{216, 5}$$

determines $\vartheta$ when $E$ is given, but we may equally legitimately regard it as determining $E$ when $\vartheta$ is given. For the reasons given in § 208 we may regard $\vartheta$ as the temperature measured on a particular scale which we call the statistical scale. We shall shortly prove that the statistical temperature $\vartheta$ is related to the temperature $T$ on the Kelvin scale by

$$\vartheta = e^{-1/kT}, \tag{216, 6}$$

where $k$ is a universal constant.

**§ 217. Degenerate systems.** The equilibrium properties of the assembly have been shown to depend only on the functions $\log(1 \pm \lambda_A \vartheta^{\epsilon_r})^{\pm 1}$, so far as concerns each set of systems. It is therefore now easy to remove the restriction to non-degenerate systems, by allowing the energies to become equal in groups of $\varpi_r$. If now the systems $A$ have degenerate states, of energy values $\epsilon_0, \epsilon_1, \ldots, \epsilon_r, \ldots$ and weights $\varpi_0, \varpi_1, \ldots, \varpi_r, \ldots$, then the average number of $A$ systems in the degenerate state $r$ is

$$\overline{n_r} = \varpi_r \lambda_A \frac{\partial}{\partial \lambda_A} \log(1 \pm \lambda_A \vartheta^{\epsilon_r})^{\pm 1} = \frac{\varpi_r}{\lambda_A^{-1} \vartheta^{-\epsilon_r} \pm 1}. \tag{217, 1}$$

The energy of these particular $A$ systems is $\overline{n_r} \epsilon_r$, or

$$\varpi_r \epsilon_r \lambda_A \frac{\partial}{\partial \lambda_A} \log(1 \pm \lambda_A \vartheta^{\epsilon_r})^{\pm 1} = \varpi_r \vartheta \frac{\partial}{\partial \vartheta} \log(1 \pm \lambda_A \vartheta^{\epsilon_r})^{\pm 1}. \tag{217, 2}$$

The average energy of all the $A$ systems is

$$\begin{aligned} \overline{E_A} &= \Sigma_r \overline{n_r} \epsilon_r = \vartheta \frac{\partial}{\partial \vartheta} \Sigma_r \varpi_r \log(1 \pm \lambda_A \vartheta^{\epsilon_r})^{\pm 1} \\ &= \Sigma_r \frac{\varpi_r \epsilon_r}{(\lambda_A \vartheta^{\epsilon_r})^{-1} \pm 1}, \end{aligned} \tag{217, 3}$$

the values of $\lambda_A$ and $\vartheta$ being fixed by the necessary equalities (216, 3) and (216, 5).

**§ 218. Classical statistical mechanics.** Non-localized systems are free to move in a common enclosure, and are distributed amongst their possible states according to (217, 1), namely

$$\overline{n_r} = \varpi_r \lambda_A \frac{\partial}{\partial \lambda_A} \log(1 \pm \lambda_A \vartheta^{\epsilon_r})^{+1} = \frac{\varpi_r \lambda \vartheta^{\epsilon_r}}{1 \pm \lambda \vartheta^{\epsilon_r}}. \tag{218, 1}$$

Let us suppose that for all $\epsilon_r$

$$\lambda_A \ll \vartheta^{-\epsilon_r}; \tag{218, 2}$$

then we may use the approximation

$$\log(1 \pm \lambda_A \vartheta^{\epsilon_r})^{\pm 1} = \lambda_A \vartheta^{\epsilon_r}, \tag{218, 3}$$

which is the first term of the expansion in series. Hence in this case both Fermi-Dirac and Bose-Einstein statistics lead to identical distributions. Using the approximation (3) we can simplify (1) to

$$\overline{n_r} = \lambda_A \varpi_r \vartheta^{\epsilon_r}. \tag{218, 4}$$

We also have then

$$N_A = \Sigma_r \overline{n_r} = \Sigma_r \lambda_A \varpi_r \vartheta^{\epsilon_r} = \lambda_A f(\vartheta), \tag{218, 5}$$

where $f(\vartheta)$ is the partition function defined in § 206. If we eliminate $\lambda_A$ between (4) and (5) we obtain

$$\overline{n_r} = N_A \varpi_r \vartheta^{\epsilon_r} / \Sigma_r \varpi_r \vartheta^{\epsilon_r} = N_A \varpi_r \vartheta^{\epsilon_r} / f(\vartheta), \tag{218, 6}$$

which is identical with (209, 2) for the distribution of localized systems.

We have thus obtained the striking result that when (2) is obeyed, the Fermi-Dirac statistics, the Bose-Einstein statistics, and the statistics for localized systems all lead to the same distribution laws. *Under these conditions we do not need to distinguish between the three kinds of statistics, and we say that the assembly obeys classical statistics.*

At the present stage we cannot say when, if ever, the condition (2) will be fulfilled. After we have related $\vartheta$ to $T$ we shall be able to show that this condition is fulfilled at all temperatures except the very lowest ($T \ll 1°$) by gaseous assemblies of any kind of ordinary chemical molecules or atoms, but not by the assembly of "free" electrons in a metal. The Fermi-Dirac statistics will be used in Chapters XI and XIV, where we sketch the electron theory of metals, but in all other applications classical statistics are an amply sufficient approximation. We shall therefore for the sake of simplicity use classical statistics throughout except in Chapters XI and XIV, but we shall first show that all three forms of statistics lead to the same thermodynamic laws.

We can anticipate the rigorous discussion of the conditions under which (2) is obeyed by a semi-quantitative physical discussion. Suppose that the total number $N_A$ of systems $A$ is much smaller than the number of possible states of not too high energy (this qualification of not too high will need to be analysed more precisely later), then the number of complexions with more than one system in any given state will be negligible compared with the number of complexions where each state contains either one system or none. We may therefore ignore the existence of conceivable complexions containing more than one system in any state. Now assemblies obeying the Fermi-Dirac statistics differ from those obeying Bose-Einstein statistics only in that complexions with more than one system in a given state are

forbidden in the former, but, if the number of such complexions is negligible anyhow, the distinction becomes unimportant. We may therefore expect the condition (2) to be closely related to the condition that the number of systems be small compared with the number of states of not too high energy. We shall later show that this is so.

**§ 219. Structureless particles moving in a box.** As an example of an assembly of type II, let us consider a number of identical structureless particles in an enclosure. The equation of Schrödinger for a structureless particle of mass $m^*$ in an enclosure of volume $V$ and uniform potential energy, which for convenience we take to be zero, is

$$\frac{\partial^2\psi}{\partial x^2}+\frac{\partial^2\psi}{\partial y^2}+\frac{\partial^2\psi}{\partial z^2}+\frac{8\pi^2 m^*}{h^2}\epsilon\psi = 0. \tag{219, 1}$$

If the enclosure has the form of a rectangular box, the eigen functions can be enumerated by means of three quantum numbers $l$, $m$, $n$ each of which can take any positive (non-zero) integral value, with the physical meaning that the squares of the momenta parallel to the edges of the box are $l^2h^2/4\pi^2$, $m^2h^2/4\pi^2$, $n^2h^2/4\pi^2$. The momenta themselves have no eigen values but an average value zero, corresponding to the fact that a particle with given $l$, $m$, $n$ is moving back and forth between the ends of the box and is as likely to be moving in one direction as in the exactly opposite direction. The energy of the state with given $l$, $m$, $n$ is

$$\epsilon_{l,m,n} = \frac{h^2}{8m^*}\left(\frac{l^2}{a^2}+\frac{m^2}{b^2}+\frac{n^2}{c^2}\right) \tag{219, 2}$$

All such states are non-degenerate. We shall here suppose that for all $\epsilon_r$

$$\lambda \ll \vartheta^{-\epsilon_r}, \tag{219, 3}$$

and shall verify afterwards that this condition is fulfilled. We therefore want to evaluate the partition function

$$f(\vartheta) = \sum_{l=1}^{\infty}\sum_{m=1}^{\infty}\sum_{n=1}^{\infty} \vartheta^{\frac{h^2}{8m^*}\left(\frac{l^2}{a^2}+\frac{m^2}{b^2}+\frac{n^2}{c^2}\right)}$$

$$= \sum_{l=1}^{\infty}\vartheta^{l^2h^2/8m^*a^2}\sum_{m=1}^{\infty}\vartheta^{m^2h^2/8m^*b^2}\sum_{n=1}^{\infty}\vartheta^{n^2h^2/8m^*c^2}. \tag{219, 4}$$

We shall further suppose and verify afterwards that

$$h^2\log(1/\vartheta)/8m^*a^2 \ll 1, \tag{219, 5}$$

$$h^2\log(1/\vartheta)/8m^*b^2 \ll 1, \tag{219, 6}$$

$$h^2\log(1/\vartheta)/8m^*c^2 \ll 1. \tag{219, 7}$$

These conditions mean that the separation of the energy states is small

compared with $1/\log(1/\vartheta)$, that is with $kT$. We may then replace the sums in (4) by integrals as in § 212, and obtain

$$f(\vartheta) = \int_0^\infty \vartheta^{h^2l^2/8m^*a^2}\,dl \int_0^\infty \vartheta^{h^2m^2/8m^*b^2}\,dm \int_0^\infty \vartheta^{h^2n^2/8m^*c^2}\,dn$$

$$= \int_0^\infty e^{-[h^2\log(1/\vartheta)/8m^*a^2]l^2}\,dl \int_0^\infty e^{-[h^2\log(1/\vartheta)/8m^*b^2]\,m^2}\,dm \int_0^\infty e^{-[h^2\log(1/\vartheta)/8m^*c^2]\,n^2}\,dn$$

$$= \left\{\frac{8m^*a^2}{h^2\log(1/\vartheta)}\frac{\pi}{4}\right\}^{\frac{1}{2}} \left\{\frac{8m^*b^2}{h^2\log(1/\vartheta)}\frac{\pi}{4}\right\}^{\frac{1}{2}} \left\{\frac{8m^*c^2}{h^2\log(1/\vartheta)}\frac{\pi}{4}\right\}^{\frac{1}{2}}$$

$$= \left\{\frac{2\pi m^*}{h^2\log(1/\vartheta)}\right\}^{\frac{3}{2}} abc = \left\{\frac{2\pi m^*}{h^2\log(1/\vartheta)}\right\}^{\frac{3}{2}} V, \qquad (219, 8)$$

$V$ being the volume of the box. Anticipating the relation between $\vartheta$ and the Kelvin temperature $T$, this becomes

$$f(\vartheta) = \frac{(2\pi m^*kT)^{\frac{3}{2}}\,V}{h^3}, \qquad (219, 9)$$

and so according to (218, 5)

$$\lambda = \frac{N}{f(\vartheta)} = \frac{N}{V}\frac{h^3}{(2\pi m^*kT)^{\frac{3}{2}}}. \qquad (219, 10)$$

We must now verify the conditions (3) and (5), (6), (7). Anticipating the relation (208, 8) between $\vartheta$ and $T$, and using the numerical values $k = 1{\cdot}37\times10^{-16}$ ergs/degree Kelvin, $h = 6{\cdot}55\times10^{-27}$ ergs $\times$ sec., $m^* = 1{\cdot}66\times10^{-24}$ g., the mass of a hydrogen atom, we find

$$h^2\log(1/\vartheta)/8m^*a^2 = h^2/8m^*a^2kT = 2{\cdot}36\times10^{-14}/a^2T. \quad (219, 11)$$

Thus for hydrogen atoms in a box with sides of length $10^{-3}$ cm. at the temperature $0{\cdot}001°$ K.

$$h^2\log(1/\vartheta)/8m^*a^2 = 2{\cdot}36\times10^{-5}, \qquad (219, 12)$$

and the conditions (5), (6), (7) are easily satisfied. They are satisfied *a fortiori* by more massive particles, a larger enclosure, or higher temperatures. Even for electrons they will usually be comfortably satisfied. We have still to verify the validity of (3) or

$$\lambda \ll e^{\epsilon_r/kT} \quad (\text{all } \epsilon_r). \qquad (219, 13)$$

Since $kT$ and all the $\epsilon_r$ are positive, (13) will be satisfied provided we can show that

$$\lambda \ll 1, \qquad (219, 14)$$

or, according to (10), that

$$\frac{N}{V}\frac{h^3}{(2\pi m^*kT)^{\frac{3}{2}}} \ll 1. \qquad (219, 15)$$

Inserting numerical values for $k$, $h$ and the value of $m^*$ for a hydrogen atom, this condition becomes

$$5{\cdot}2 \times 10^{-21} \frac{N}{V} \frac{1}{T^{\frac{3}{2}}} \ll 1. \tag{219, 16}$$

The molecular density in an ordinary gas at standard temperature and pressure gives $N/V = 2{\cdot}7 \times 10^{19}$. For the same concentration and $T = 9^\circ$ K., the left side of (16) becomes 0·005 and the condition is well satisfied. *A fortiori* $\lambda$ will be much smaller than 1 for more massive particles, higher temperatures or smaller concentrations. Thus in applications to actual gases we may assume that $\lambda$ is small, and we may use classical statistics. The only important exception will be an assembly of electrons at the concentrations at which one would expect to find free electrons in metals, about one per atom. On account of the much smaller mass of the electron, in such assemblies $\lambda \gg 1$ even up to temperatures greater than 2000° K. The formulae of this paragraph are then not applicable.

We shall return in Chapter III to assemblies of the type discussed in this section and shall there discuss them from a more familiar point of view.

**§ 220. External reactions of the assembly.** In addition to the foregoing formulae for the distribution laws we require formulae for the average (equilibrium) values of the forces exerted by the assembly, or its sets of systems, on the bodies which control the geometry of the assembly. The most important example is the formula for the pressure of a gas.

We may assume that the states of any system in the assembly (or of the assembly itself) are determined by solving Schrödinger's equation with a potential energy which is itself a function of certain parameters $x_1, x_2, \ldots$, defining the positions of all the external bodies. The energies $\epsilon_r$ of the possible states of any system are then functions of $x_1, x_2, \ldots$. The weights $\varpi_r$ are, however, constants, as they are necessarily merely the number of independent solutions for a given value of the energy and given $x$'s. They could at most only change discontinuously for certain values of the $x$'s, and if the potential energy is a continuous function of the $x$'s this is impossible.

It will be observed that we have here classified the universe into two parts, the assembly in which we are interested, and the rest of the universe. This is an essential part of any discussion of external reactions and, of course, what part of the universe we call the assembly can always be chosen at our own discretion. Now the assembly and any one of the bodies which produce the external field also form together a quantal system, in which if undisturbed the energy must be conserved. When therefore a relevant parameter $x$, defining the position of this body, is allowed to change by an amount $dx$, the system in the original assembly remaining in its original

state $r$, energy must be conserved. The energy of the state will have increased by $d\epsilon_r$, and we express this conservation by saying that the system has done *work* on the external body to an amount $-d\epsilon_r$. This is more conveniently expressed by saying that the system exerts a generalized force component $X_r$ on the external body, such that in any infinitesimal displacement in which the system remains in its original state $r$ (reversible displacement) the work done is $X_r dx$ where

$$X_r = -\partial\epsilon_r/\partial x. \tag{220, 1}$$

In any state of the assembly it follows that the total generalized force $X$ due to one set of systems and tending to increase the parameter $x$ is given by

$$X = -\Sigma_r n_r \partial\epsilon_r/\partial x. \tag{220, 2}$$

There are similar generalized forces for other states and other parameters. The average value of this force which the assembly will exert in its equilibrium state is therefore

$$X = -\Sigma_r \overline{n_r} \partial\epsilon_r/\partial x. \tag{220, 3}$$

Using (217, 1) for $n_r$ this becomes

$$\overline{X} = -\Sigma_r \frac{\partial\epsilon_r}{\partial x}\varpi_r\lambda\frac{\partial}{\partial\lambda}\log(1\pm\lambda\vartheta^{\epsilon_r})^{\pm 1} = -\Sigma_r \frac{\partial\epsilon_r}{\partial x}\frac{\varpi_r\lambda\vartheta^{\epsilon_r}}{1\pm\lambda\vartheta^{\epsilon_r}}. \tag{220, 4}$$

§ 221. **Relationship between statistical mechanics and thermodynamics.** We have now obtained all the distribution laws of the equilibrium (average) state of any assembly of systems, between which the energy of interaction is negligible. We shall later extend these laws to apply to assemblies of interacting systems. Before doing so it is of interest to consider the relation between the laws already derived and classical thermodynamics. We have obtained all these distribution laws without any reference to thermodynamical ideas, except to point out that there must be a universal relation between $\vartheta$ and the absolute temperature. The ideas of thermodynamics are entirely foreign to the *foundations* of statistical mechanics, which are mainly dynamical. The proper course is to prove that the laws of thermodynamics are true for the assemblies of statistical mechanics, if we use suitable analogies to interpret the properties of these assemblies.* Such proofs are given in the succeeding sections, and it will be seen that the direct introduction of the laws of thermodynamics in this way is satisfactorily simple.

§ 222. **The laws of thermodynamics.** Since the basic laws of thermodynamics can be formulated in several alternative ways, it will be necessary for us to describe shortly the basis which we actually adopt, because the development of the relationship with statistical mechanics is naturally

* This was made abundantly clear by Gibbs, *Collected Works*, 2 *Elementary Principles in Statistical Mechanics*, Chapters IV and XIV (Longmans, 1928)

somewhat affected by this choice. The most logically satisfactory formulation is undoubtedly that of Caratheodory.* We shall not quote this formulation as it is rather too abstract, but shall give a less abstract formulation easily derived from Caratheodory's. This formulation we may call the classical formulation, being the one most commonly adopted, although some of the postulates are often assumed without being explicitly stated. This classical formulation is, however, not the formulation which is most simply related to the statistical laws which we have obtained. We therefore give after the classical formulation another variant, which is derivable from the classical formulation, is as useful as the classical formulation, and is more conveniently related to the statistical laws.

We shall, for the sake of brevity, omit definitions of "thermodynamic state", "work", "thermal insulation", "adiabatic", "thermal contact", "thermal equilibrium", but must emphasize that these can be defined without any reference to temperature.

The first step is to introduce the concept of temperature. As a natural generalization of experience we introduce the postulate: *If two assemblies are each in thermal equilibrium with a third assembly, they are in thermal equilibrium with each other.* From this it may be shown to follow that the condition for thermal equilibrium between several assemblies is the equality of a certain single-valued function of the thermodynamic states of the assemblies, which may be called the temperature $t$, any one of the assemblies being used as a "thermometer" reading the temperature $t$ on a suitable scale. This postulate of the "*Existence of temperature*" could with advantage be known as *the zeroth law of thermodynamics*. This temperature, whose existence is thus postulated, is measured on a scale which is determined only by the arbitrary choice of the thermometer system, and is called *the empirical temperature* when it is necessary to distinguish it from the absolute temperature defined later. For example, the empirical temperature $t$ might be defined to be the measured volume of a constant quantity of any chosen substance at constant pressure.

We now formulate the First Law of Thermodynamics as follows. *If a thermally insulated assembly can be taken from a state I to a state II by alternative paths, the work $w$ done on the assembly has the same value for every such (adiabatic) path.* From this one can deduce that there exists a single-valued function $E$ of the state of an assembly, called its total energy, such that for any adiabatic process the increase $\Delta E$ of the energy is equal to the work done on the assembly. Thus

$$\Delta E = w \quad \text{(adiabatic process).} \tag{222, 1}$$

* Caratheodory, *Math. Ann.* **67**, 355 (1909). For a simple account see Born, *Physikal. Zeit.* **22**, 218, 249, 282 (1921).

In particular in an assembly mechanically as well as thermally isolated the energy remains constant, thus

$$\Delta E = 0 \quad \text{(isolated assembly)}. \qquad (222, 2)$$

It follows that in any interaction between two parts of an isolated assembly gain of energy in the one part is equal to the loss of energy in the other. It is to be noticed that for this definition of energy it is necessary and sufficient that it be possible by an adiabatic process to change the assembly either from state I to state II or from state II to state I.

We now define the heat $q$ absorbed by an assembly as the increase in total energy of the assembly less the work done on the assembly, thus

$$q = \Delta E - w \quad \text{(all processes)}. \qquad (222, 3)$$

We now formulate the Second Law of Thermodynamics as follows. *There exist single-valued functions of state, $T$, called the absolute temperature, and $S$, called the entropy, such that*

(1) *$T$ is a function of $t$ only.*

(2) *The entropy of any assembly is equal to the sum of the entropies of its parts.*

(3) *For any infinitesimal change in any completely homogeneous assembly*

$$q \leqslant T\,dS; \qquad (222, 4)$$

*the equality sign holds for quasi-static processes, the inequality for natural (irreversible) processes. If an assembly is not completely homogeneous, the relation* (4) *applies to each of its homogeneous parts.*

These postulates form a sufficient basis of thermodynamics. From them one can, for instance, immediately derive Carnot's formula for the efficiency of a reversible cycle.* Actually we shall have more use for the branch of thermodynamics which gives us the conditions for complete equilibrium. We shall briefly outline the procedure for deriving these conditions from the postulates.

If an assembly is in complete equilibrium, then every conceivable infinitesimal change must be quasi-static. The condition for complete equilibrium is therefore by (4) that for every infinitesimal process

$$q = T\,dS \quad \text{(equilibrium)}. \qquad (222, 5)$$

If we combine this with (3) the condition becomes

$$T\,dS = dE - w \quad \text{(equilibrium)}. \qquad (222, 6)$$

Certain special forms of (6) are of particular importance. We quote two.

* For this derivation see, for example, *M.T.* p. 6.

For an assembly isolated thermally and mechanically

$$w = 0, \quad dS = 0, \quad dE = 0 \quad \text{(equilibrium)}. \tag{222, 7}$$

For an assembly mechanically isolated in a thermostat

$$w = 0, \quad dT = 0, \quad d(E-TS) = 0 \quad \text{(equilibrium)}. \tag{222, 8}$$

The quantity $E-TS$ occurring in (8) is called the free energy, and is denoted by $F$. It plays a fundamental part in the alternative formulation given below, and in our derivation of the laws of thermodynamics from those of statistical mechanics.

This completes the classical formulation. To make use of it one proceeds as follows. One assumes that any assembly, if not completely homogeneous, can be divided into a number of completely homogeneous parts called phases each with its own energy, entropy and temperature. The energy and entropy of the whole assembly are then equal to the sum of those of the constituent phases. A complete description of the state of the whole assembly involves a complete description of each phase. To define completely a given phase we first define its composition, that is the number $N_A, N_B, \ldots$ of the various types of systems (molecules) that it contains. Next we specify the values of all geometrical parameters $x$. [Usually the only important one in practice is the volume $V$.] Having done this the phase still has one degree of freedom and we require to specify one further quantity to complete the description of its state. In the classical formulation the quantity chosen is the entropy. We thus have for the given phase the independent variables $S, x_1, \ldots, N_A, N_B, \ldots$ or for brevity $S, x, N$. Any other property of the phase may then be regarded as a function of $S$, $x$, $N$, and in particular the total energy may be so regarded. We may therefore write for any variation in the state or nature of the phase

$$dE = \frac{\partial E}{\partial S} dS + \Sigma \frac{\partial E}{\partial x} dx + \Sigma \frac{\partial E}{\partial N} dN. \tag{222, 9}$$

If in particular we consider a variation at constant configuration and constant composition, (9) reduces to

$$dE = \left(\frac{\partial E}{\partial S}\right)_{x, N} dS \quad (x, N \text{ constant}), \tag{222, 10}$$

and $E$ becomes a single-valued function of $S$. The only process that can take place at constant configuration and constant composition is an absorption of heat, for at constant configuration there can be no work.* In this case (3) reduces to

$$q = dE. \tag{222, 11}$$

* It must be remembered that constant configuration includes constancy of any long-range fields produced by bodies outside the assembly.

Substituting (11) into (10) we obtain

$$q = \left(\frac{\partial E}{\partial S}\right)_{x,N} dS. \tag{222, 12}$$

If we arrange that the absorption of heat be quasi-static we have according to (4)

$$q = TdS, \tag{222, 13}$$

and so by comparison of (12) and (13)

$$\left(\frac{\partial E}{\partial S}\right)_{x,N} = T. \tag{222, 14}$$

Since for given $x$, $N$ we know that $E$ is a single-valued function of $S$, the relation (14) must be independent of the process used in its derivation. We may then rewrite (9) as

$$dE = TdS + \Sigma \frac{\partial E}{\partial x} dx + \Sigma \frac{\partial E}{\partial N} dN. \tag{222, 15}$$

Provided the phase is in mechanical equilibrium with its surroundings, $-(\partial E/\partial x)$ is simply the generalized mechanical force exerted by the phase tending to increase $x$. This we denote by $X$. The coefficients $\partial E/\partial N$ are the quantities introduced by Gibbs and denoted by $\mu$. We call them the partial potentials. Introducing these symbols we rewrite (15) as

$$dE = TdS - \Sigma X dx + \Sigma \mu dN. \tag{222, 16}$$

This formula shows the dependence of $E$ on the independent variables $S$, $x$, $N$; $E$, thus regarded as a function of these variables, is called the thermodynamic potential for the variables $S$, $x$, $N$. Formula (16) is called the fundamental formula* for this set of independent variables. There is one such formula for each phase. These formulae form the usual starting-point for determining equilibrium properties after the manner of Gibbs.

By using fundamental formulae of the type (16), one such for each phase, one can deduce

(*a*) That heat flows always from a higher temperature to a lower one.

(*b*) That any geometrical boundary moves from a higher pressure to a lower one.

(*c*) That chemical changes always proceed in such a direction that certain linear combinations of the partial potentials decrease.

As a corollary of (*a*) we have the fact that there is thermal equilibrium between two phases of equal temperature, which is already known from the zeroth law. Since we are mainly interested in the equilibrium properties of assemblies, we can dispense with deduction (*a*) and confine ourselves to assemblies of uniform temperature. We can then transform the formulation

* See Gibbs' *Collected Works*, **1**, 88, footnote (Longmans, 1928).

of the second law to a more convenient form, which is less general than the classical formulation, but only to the trivial extent that one postulates equality of temperature throughout the assembly.*

Adopting this standpoint we are able in our choice of independent variables to replace the entropies of each of the phases by the temperature of the whole assembly. The whole formulation can thereby be simplified. To achieve this we define the free energy $F$ by

$$F = E - TS, \tag{222, 17}$$

and differentiating (17) and combining the result with (16) we obtain

$$dF = -SdT - \Sigma X dx + \Sigma \mu dN. \tag{222, 18}$$

Formula (18) is the fundamental formula for the variables $T$, $x$, $N$; $F$ is the thermodynamic potential for these variables. One could, if one wished, use formula (18) as the basis of the second law. The variables $T$, $x$, $N$ are indeed, from the statistical point of view, more "natural" than $S$, $x$, $N$, but we can improve the naturalness still further by getting rid of all need to refer to $S$. This we now proceed to do.

According to (18) we have

$$\frac{\partial F}{\partial T} = -S, \tag{222, 19}$$

and consequently, by using (17) with (19)

$$\frac{\partial (F/T)}{\partial T} = \frac{1}{T}\frac{\partial F}{\partial T} - \frac{F}{T^2} = -\frac{TS+F}{T^2} = -\frac{E}{T^2}. \tag{222, 20}$$

By using (20) we can eliminate $S$ from (18) and obtain

$$d\left(\frac{F}{T}\right) = -\frac{E}{T^2}dT - \frac{1}{T}\Sigma X dx + \frac{1}{T}\Sigma \mu dN. \tag{222, 21}$$

It is this formula which we choose to adopt as our basis for the alternative version of the second law. We now proceed to give our alternative formulation.

The zeroth law, the first law, and the definition of heat are preserved in the form already given. It is only in the formulation of the second law that there is a departure from the classical formulation. The formulation of the second law which we now adopt is the following.

*Second Law (alternative formulation). There exist single-valued functions of state, $T$, called the absolute temperature, and $F$, called the free energy, such that*

(1) *$T$ is a function of $t$ only.*

(2) *The free energy of an assembly is equal to the sum of the free energies of its parts.*

* Cf. Gibbs' *Collected Works*, 1, 90, footnote (Longmans, 1928).

(3) *When work w is done on the assembly isothermally*

$$dF \leqslant w \quad (dT = 0); \tag{222, 22}$$

*the equality sign refers to quasi-static processes, and the inequality sign to actual (natural) processes.*

(4) *When F is regarded as a function of T, x, N, its dependence on the temperature is given by*

$$\frac{\partial(F/T)}{\partial T} = -\frac{E}{T^2}. \tag{222, 23}$$

Adopting this formulation we need indicate, only quite briefly, how it leads to the same equilibrium laws as the classical formulation. Choosing the independent variables $T$, $x$, $N$ we write

$$d\left(\frac{F}{T}\right) = \frac{\partial(F/T)}{\partial T}\,dT + \frac{1}{T}\Sigma\frac{\partial F}{\partial x}\,dx + \frac{1}{T}\Sigma\frac{\partial F}{\partial N}\,dN. \tag{222, 24}$$

The coefficient of $dT$ is determined by (23). Formula (22), applied to quasi-static variations of the geometry* of the assembly at fixed composition, tells us that $-\partial F/\partial x = X$. Alternatively we may take this as the definition of the generalized forces $X$. Finally we define the partial potentials $\mu$ by the relation

$$\mu_i = \left(\frac{\partial F}{\partial N}\right)_{T,\,x,\,n_j\,(j \neq i)} \tag{222, 25}$$

We thus have
$$d\left(\frac{F}{T}\right) = -\frac{E}{T^2}\,dT - \frac{1}{T}\Sigma X\,dx + \frac{1}{T}\Sigma\mu\,dN, \tag{222, 26}$$

or alternatively
$$Td\left(\frac{F}{T}\right) = -\frac{E}{T}\,dT - \Sigma X\,dx + \Sigma\mu\,dN, \tag{222, 27}$$

in agreement with formula (21) obtained by the classical derivation.

The condition for complete equilibrium of an assembly is that any change whatever should be quasi-static, and according to (22) this can be formulated as

$$dT = 0, \quad dF = w \quad \text{(equilibrium)}, \tag{222, 28}$$

and in particular, considering chemical changes, keeping the geometry of the assembly unaltered,

$$dT = 0, \quad dx = 0, \quad dF = 0 \quad \text{(equilibrium)}. \tag{222, 29}$$

Formula (29) is the most convenient general form for the conditions of chemical equilibrium.

It is not essential to introduce other thermodynamic functions than $E$, $F$, $T$, $\mu$, which are now defined. For completeness, however, we can define the entropy $S$ by

$$S = (E - F)/T. \tag{222, 30}$$

* Including variations of long range fields.

We then have
$$\frac{\partial F}{\partial T} = T\frac{\partial(F/T)}{\partial T} + \frac{F}{T} = -\frac{E}{T} + \frac{F}{T} = -S, \qquad (222, 31)$$

using (23) and (30). Alternatively we might define $S$ by (31) and deduce (30). Apart from the arbitrariness in the units in which $E$, $F$, $T$ and $S$ are measured and the arbitrary zero from which $E$ and $S$ are measured, $E$, $T$, $F$, $S$ are unique. The arbitrary constant term $a$ in $S$ appears in $F$ in the form $aT$. This term cannot affect any of the specified properties of $F$ and so has no physical significance.

**§ 223. Derivation of thermodynamics from statistical mechanics.** We have already found the correct analogy to the zeroth law, since $\vartheta$ has the required properties of temperature. The first law is also an obvious deduction from our premises, if we define the total energy $E$ of thermodynamics by the equation

$$E = \overline{E} = \Sigma_A \overline{E_A} = \Sigma_A \Sigma_r \overline{n_r} \epsilon_r. \qquad (223, 1)$$

To deduce the second law in the required form we have to define suitable functions to act as $T$ and $F$. We shall show that this can be done. Since $\vartheta$ may be identified as the empirical temperature, we may tentatively define $T$ by

$$kT = \frac{1}{\log(1/\vartheta)}, \qquad (223, 2)$$

where $k$ is any constant, merely fixing the size of the degree. We then define $F$ by the equations

$$F = \Sigma_A F_A, \qquad (223, 3)$$

$$F_A \log\vartheta = -\frac{F_A}{kT} = \Sigma_r \varpi_r \log(1 \pm \lambda_A \vartheta^{\epsilon_r})^{\pm 1} - N_A \log\lambda_A. \qquad (223, 4)$$

We have now to show that $F$ and $T$ have the properties of free energy and absolute temperature respectively, required by the adopted version of the second law. The additive property of the free energy is already catered for by the form of the definition (3).

To derive the other required properties of $F$ we have to treat $F$ as a function of $\vartheta$ (or $T$), $x$ and $N_A$. We therefore note that $\lambda_A$ depends on $\vartheta$, $x$ and $N_A$, while $\epsilon_r$ depends on $x$ only. The complete differential of $F_A \log\vartheta$ is then

$$d(F_A \log\vartheta) = \frac{\partial(F_A \log\vartheta)}{\partial\log\vartheta} d\log\vartheta + \log\vartheta\, \Sigma_r \frac{\partial F_A}{\partial\epsilon_r}\frac{\partial\epsilon_r}{\partial x} dx + \log\vartheta \frac{\partial F_A}{\partial N_A} dN_A$$
$$+ \log\vartheta \frac{\partial F_A}{\partial\lambda_A}\left\{\frac{\partial\lambda_A}{\partial\log\vartheta} d\log\vartheta + \frac{\partial\lambda_A}{\partial x} dx + \frac{\partial\lambda_A}{\partial N_A} dN_A\right\}. \qquad (223, 5)$$

We require next the value of $\partial F_A/\partial\lambda_A$ to insert into (5). From (4) we deduce

$$\lambda_A \log\vartheta \frac{\partial F_A}{\partial\lambda_A} = \Sigma_r \frac{\varpi_r}{\lambda_A^{-1}\vartheta^{-\epsilon_r} \pm 1} - N_A = \Sigma_r \overline{n_r} - N_A = 0. \qquad (223, 6)$$

using (217, 1).* Consequently in (5) we may omit all terms containing $\partial F_A/\partial\lambda_A$ as a factor and treat $\lambda_A$ as though it were not variable, so that (5) simplifies to

$$d(F_A \log\vartheta) = \frac{\partial(F_A \log\vartheta)}{\partial \log\vartheta} d\log\vartheta + \log\vartheta\, \Sigma_r \frac{\partial F_A}{\partial\epsilon_r}\frac{\partial\epsilon_r}{\partial x} dx + \log\vartheta \frac{\partial F_A}{\partial N_A} dN_A, \tag{223, 7}$$

*all differentiations being performed treating $\lambda_A$ as constant.* If we now compare (4) with (217, 3) we obtain

$$\left(\frac{\partial[F_A \log\vartheta]}{\partial \log\vartheta}\right)_{x,N_A} = \left(\frac{\partial[F_A \log\vartheta]}{\partial \log\vartheta}\right)_{x,N_A,\lambda_A} = \vartheta\frac{\partial}{\partial\vartheta}\Sigma_r \varpi_r \log(1 \pm \lambda_A \vartheta^{\epsilon_r})^{\pm 1} = E_A. \tag{223, 8}$$

Similarly by comparing (4) with (220, 4) we obtain

$$\left(\frac{\partial F_A}{\partial x}\right)_{\vartheta,N} = \Sigma_r\left(\frac{\partial F_A}{\partial\epsilon_r}\right)_{\vartheta,N_A,\lambda_A}\frac{\partial\epsilon_r}{\partial x} = \Sigma_r \frac{\varpi_r\lambda_A\vartheta^{\epsilon_r}}{1 \pm \lambda_A\vartheta^{\epsilon_r}}\frac{\partial\epsilon_r}{\partial x} = -\bar{X}. \tag{223, 9}$$

Further from (4) we derive

$$\left(\frac{\partial F_A}{\partial N_A}\right)_{\vartheta,x} = \left(\frac{\partial F_A}{\partial N_A}\right)_{\vartheta,x,\lambda_A} = -\frac{\log\lambda_A}{\log\vartheta}. \tag{223, 10}$$

Hence substituting (8), (9) and (10) into (7) and summing for all species, we obtain using (3)

$$d(F\log\vartheta) = E\,d\log\vartheta - \log\vartheta\,\Sigma\,\bar{X}\,dx - \Sigma_A \log\lambda_A\, dN_A. \tag{223, 11}$$

We now substitute from (2), which tentatively defined $T$ as a certain function of $\vartheta$, and obtain

$$d\left(\frac{F}{T}\right) = -\frac{E}{T^2}dT - \frac{1}{T}\Sigma\,\bar{X}\,dx + k\,\Sigma_A \log\lambda_A\, dN_A. \tag{223, 12}$$

If now we compare formula (12) obtained statistically, by using the tentative definitions (2), (3) and (4) of $T$ and $F$, with the thermodynamic formula (222, 26), we find that the dependence of $F$ on $T$ and $x$ is identical in the two formulae, provided we identify $E$ with $\bar{E}$ and $X$ with $\bar{X}$. This partly justifies our identification of $T$ and $F$ defined according to (2), (3) and (4) with the thermodynamic temperature and free energy respectively. To complete the justification for this identification we must show that the terms of (12) and (222, 26) in $dN_A$ are also equivalent to each other. We can tentatively make these terms equivalent by assuming that each $\lambda$ is related to a partial potential $\mu$ according to a relation of the form

$$\mu_A = kT\log\lambda_A, \tag{223, 13}$$

or

$$\lambda_A = e^{\mu_A/kT}. \tag{223, 14}$$

We shall show that these relationships between the statistical $\lambda$'s and the

* The reader who has followed the reasoning summarized in § 215 will be able to verify that the relation $\partial F_A/\partial\lambda_A = 0$ follows from the definition of $\lambda_A$ as the value of a coordinate at a col.

thermodynamic $\mu$'s are correct, and thus complete the justification for our assumption that $F$ defined by (3) and (4) is identical with the thermodynamic free energy.

The criterion for the correctness of the tentative identification (13) or (14) is that the same conditions for complete equilibrium should be obtained by the statistical method as by the thermodynamic. We cannot at this stage give the most general proof of this, but in effect there are only two independent types of equilibria of importance, namely the equilibrium for a particular kind of system partitioned between several parts (phases) of the assembly (physical phase equilibrium), and that for the interconversion of different types of systems (chemical equilibrium). We shall now show that (14) leads correctly to the conditions for physical phase equilibrium; we postpone consideration of chemical equilibrium to Chapter v.

Let us examine first the statistical condition for equilibrium in a two-phase assembly. In all our derivations the subscripts $A$, $B$, ... each referred to a set of identical systems, that is systems which have the same accessible states. This means that all the $A$'s must be not only chemically identical but in the same enclosure. If we have two sets of systems of identical chemical nature but confined to different enclosures (phases) in thermal contact, then all our formulae are applicable to the assembly consisting of the two enclosures, provided we denote the two separate sets of chemically similar systems by different symbols $A$, $A'$, $B$, $B'$, and so on. The two parts of the assembly will have a common temperature ($\vartheta$ or $T$), but there will in general be different values of the $\lambda$'s in the separate enclosures, say $\lambda_A$, $\lambda_B$, ... in the one and $\lambda'_A$, $\lambda'_B$, ... in the other. Suppose now that we replace the barrier by a membrane permeable only to the systems $A$ (including, of course, $A'$). The $A$'s and $A'$'s redistribute themselves until equilibrium is reached. Only in the special case that the two enclosures (phases) were already in equilibrium, will no change take place. But when all the states primed and unprimed are accessible to all the systems of type $A$, statistical theory requires that there must be a common value of $\lambda_A$ for all the systems $A$ whichever enclosure they happen to be in. Hence in the special case that no change takes place when the barrier is removed, we know that $\lambda_A$ must have already had the same value in both enclosures before the barrier was removed. Thus the condition for equilibrium between the two enclosures (phases) with respect to the system $A$ is

$$\lambda'_A = \lambda_A. \qquad (223,15)$$

There will be a similar equilibrium condition for each other chemical species $B$, $C$, .... We shall in Chapter v give a somewhat different derivation of the equilibrium condition (15).

We can now show that the statistical condition expressed by (15) is equivalent to the thermodynamic condition. We saw in § 222 that the thermodynamic condition for complete equilibrium could be expressed in the form (222, 29). In the present example the process to be considered is the transfer, at constant temperature and constant geometry, of some of the single species $A$ from one of the two phases to the other. For this simple process the conditions (222, 29) reduce to

$$\mu_A dN_A + \mu'_A dN'_A = 0, \tag{223, 16}$$

subject to

$$dN_A + dN'_A = 0, \tag{223, 17}$$

the primed symbols referring to the second phase. We can eliminate $dN_A$, $dN'_A$ from (16) and (17) and so obtain as the *thermodynamic* condition for equilibrium between two phases the form

$$\mu'_A = \mu_A. \tag{223, 18}$$

If now the $\lambda$'s and $\mu$'s are related according to (13) we may replace (18) by

$$\lambda'_A = \lambda_A, \tag{223, 19}$$

in agreement with the *statistical* condition (15). We have thus shown that the same condition (15) or (19) for the (physical) equilibrium of a given type of system between two phases is obtained both from statistical laws and from the thermodynamic law of making $F$ minimum for given $T$, $x$. In Chapter v we shall show that both laws lead to the same conditions for homogeneous chemical equilibrium. But the most general kind of physico-chemical equilibrium can be derived by superposition of these two types of equilibrium. We may thus be assured that $F$ defined by (3) and (4) has all the essential properties of the thermodynamic free energy, and so comparison of (12) and (222, 26) shows that the statistical and thermodynamic temperature scales are correctly related by (2).

Proceeding thus we have definitely discarded Boltzmann's hypothesis* relating entropy to probability as a basis for the relationship in this connection. Boltzmann's hypothesis then becomes a theorem which can be derived from the chosen basis at a later stage.

**§ 224. Thermodynamic transcription.** Having now established the complete equivalence of the equilibrium laws derivable from statistical mechanics and from thermodynamics, we are justified in making full use of thermodynamic formulae wherever convenient. It is therefore expedient to recapitulate the relations between the statistical and thermodynamic

* For a detailed criticism of Boltzmann's hypothesis see *S.M* §§ 6 8, 6·9.

functions. First we have the relation between the two temperature scales

$$\vartheta = e^{-1/kT}, \tag{224, 1}$$

or

$$T = \frac{1}{k\log(1/\vartheta)}. \tag{224, 2}$$

The thermodynamic total energy $E$ is simply equal to the statistical average energy $\bar{E}$, while the free energy can, according to (220, 4) and (223, 12), be regarded as the potential of the average force for isothermal changes. Thus we have the strikingly simple relations

$$E = \bar{E}, \tag{224, 3}$$

$$\frac{\partial F}{\partial x} = \overline{\frac{\partial E}{\partial x}} = -\bar{X}. \tag{224, 4}$$

If we substitute (1) into (223, 4) we obtain

$$F_A = -kT\,\Sigma_r\,\varpi_r \log(1 \pm \lambda_A e^{-\epsilon_r/kT})^{\pm 1} + N_A kT \log\lambda_A, \tag{224, 5}$$

while $F$ is given by

$$F = \Sigma_A F_A. \tag{224, 6}$$

Similarly substituting (1) and (3) into (217, 3) we obtain

$$E_A = -T^2\frac{\partial(F_A/T)}{\partial T} = \Sigma_r \frac{\varpi_r \epsilon_r}{e^{\epsilon_r/kT}/\lambda_A \pm 1}, \tag{224, 7}$$

while $E$ is given by

$$E = \Sigma_A E_A. \tag{224, 8}$$

We also have the relation between the statistical parameters $\lambda_A$ and the partial potentials* $\mu_A$

$$\mu_A = kT\log\lambda_A. \tag{224, 9}$$

An appropriate thermodynamic name for $\lambda_A$ is the *absolute activity* of $A$, to distinguish it from the *relative activity*† $a_A$ defined by

$$\mu_A = \mu_A^0(T) + kT\log a_A, \tag{224, 10}$$

where $\mu_A^0(T)$ is arbitrarily fixed at each temperature. The condition for heterogeneous equilibrium of systems of type $A$ between two parts I and II of an assembly can then be expressed in the equivalent forms

$$\mu_A^{\rm I} = \mu_A^{\rm II}, \tag{224, 11}$$

$$\lambda_A^{\rm I} = \lambda_A^{\rm II}. \tag{224, 12}$$

* For uncharged systems in the absence of any external field $\mu_A$ may be called the chemical potential, but for electrically charged systems $\mu_A$ here denotes the electrochemical potential denoted in *M.T.* by $\bar{\mu}_A$ and in a gravitational field our $\mu_A$ denotes the (chemical + gravitational) potential denoted in *M.T.* by $(\mu_A + M\phi)$. The present notation seems more logical than that used in *M.T.* and the expression partial potential should be unambiguous.

† Lewis and Randall, *Thermodynamics*, p. 255 (McGraw-Hill, 1923).

These relations between the statistical quantities and the thermodynamic quantities lead, as we have already shown, to the thermodynamic formula

$$d\left(\frac{F_A}{T}\right) = -\frac{E_A}{T^2}dT - \frac{1}{T}\Sigma X_A dx + \frac{1}{T}\mu_A dN_A, \qquad (224, 13)$$

or by summation over all types of systems

$$d\left(\frac{F}{T}\right) = -\frac{E}{T^2}dT - \frac{1}{T}\Sigma X dx + \frac{1}{T}\Sigma \mu dN. \qquad (224, 14)$$

As already described in § 222 we can now define the entropy $S$ by

$$S = \Sigma S_A, \qquad (224, 15)$$

$$S_A = (E_A - F_A)/T, \qquad (224, 16)$$

and deduce that

$$\left(\frac{\partial F_A}{\partial T}\right)_{x, N_A} = -S_A. \qquad (224, 17)$$

By combining (16) with (5) and (7) we obtain as the statistical formula for the entropy of the systems $A$

$$S_A = k\Sigma_r \varpi_r \log(1 \pm \lambda_A e^{-\epsilon_r/kT})^{\pm 1} + \frac{1}{T}\Sigma_r \frac{\varpi_r \epsilon_r}{e^{\epsilon_r/kT}/\lambda_A \pm 1} - N_A k \log \lambda_A. \qquad (224, 18)$$

**§ 225. Thermodynamic formulae of classical statistics.** We have shown that both Fermi-Dirac and Bose-Einstein statistics lead to the same thermodynamic laws. Since the statistical formulae for localized systems can be derived formally as a limiting case of either the Fermi-Dirac or the Bose-Einstein formulae by assuming $\lambda \ll 1$, it is evident that this third form of statistics also leads to the same thermodynamic laws. We have already mentioned that for almost all assemblies the condition $\lambda \ll 1$ is satisfied, and the three forms of statistics take the common form of classical statistics. We then have with sufficient accuracy

$$\log(1 \pm \lambda_A e^{-\epsilon_r/kT})^{\pm 1} = \lambda_A e^{-\epsilon_r/kT}, \qquad (225, 1)$$

and (224, 5) reduces to

$$F_A = -kT\lambda_A f_A(T) + N_A kT \log \lambda_A. \qquad (225, 2)$$

But by (218, 5)

$$\lambda_A = N_A/f_A(T). \qquad (225, 3)$$

Substituting (3) into (2) we obtain

$$F_A = -N_A kT\{\log f_A(T) - \log N_A + 1\}. \qquad (225, 4)$$

Differentiating (4) with respect to $N_A$ and using the definition of $\mu_A$ in (222, 25) we obtain

$$\mu_A = kT \log \frac{N_A}{f_A(T)}, \qquad (225, 5)$$

which could alternatively be obtained by substituting (3) into (224, 9).

We shall continually make use of (4) and (5). Most of this book will be concerned with the evaluation of the partition functions $f_A(T)$ for various types of assembly. Once the partition functions are known we can construct the free energy of the assembly by means of (4). We can then derive any required equilibrium properties by the usual thermodynamic formulae. For instance, for the energy $E_A$, we obtain from (4)

$$E_A = \frac{\partial(F_A/T)}{\partial(1/T)} = N_A kT^2 \frac{\partial \log f_A(T)}{\partial T}, \qquad (225, 6)$$

while for the generalized force $X$ corresponding to the coordinate $x$ we find

$$X = -\frac{\partial F_A}{\partial x} = N_A kT \frac{\partial \log f_A(T)}{\partial x}. \qquad (225, 7)$$

The contribution $C_A^{(x)}$ of the systems $A$ to the heat capacity of the assembly, for constant geometrical parameters $x$, is defined by

$$C_A^{(x)} = \partial E_A/\partial T. \qquad (225, 8)$$

Substituting from (6) into (8), we obtain

$$C_A^{(x)} = N_A k \frac{\partial}{\partial T}\left(T^2 \frac{\partial \log f_A(T)}{\partial T}\right)$$

$$= N_A k \left(\frac{1}{T}\right)^2 \frac{\partial^2 \log f_A(T)}{\partial (1/T)^2}. \qquad (225, 9)$$

§ **226. Boltzmann's constant and the gas constant.** The constant $k$ merely fixes the size and sign of the degree on the $T$ scale. We shall discuss first the sign. If we expand $f_A(T)$ in formula (225, 9) and perform the differentiation, we obtain

$$\frac{C_A^{(x)}}{N_A k} = \left(\frac{1}{T}\right)^2 \frac{\partial^2}{\partial (1/T)^2}\{\log \Sigma_r \varpi_r e^{-\epsilon_r/kT}\}$$

$$= \frac{1}{k^2 T^2}\left[\frac{\Sigma_r \varpi_r \epsilon_r^2 e^{-\epsilon_r/kT}}{\Sigma_r \varpi_r e^{-\epsilon_r/kT}} - \left(\frac{\Sigma_r \varpi_r \epsilon_r e^{-\epsilon_r/kT}}{\Sigma_r \varpi_r e^{-\epsilon_r/kT}}\right)^2\right]$$

$$= \frac{1}{k^2 T^2} \frac{\Sigma_r \Sigma_s \varpi_r \varpi_s (\epsilon_r - \epsilon_s)^2 e^{-(\epsilon_r + \epsilon_s)/kT}}{(\Sigma_r \varpi_r e^{-\epsilon_r/kT})^2} \geqslant 0. \qquad (226, 1)$$

The universal convention for the absolute temperature is that $\bar{E}$ increases as $T$ increases; consequently we must choose $k$ positive.

The Kelvin scale of temperature $T$ is obtained by adjusting the value of $k$ so that 100 degrees separate the ice-point and the steam-point (at one atmosphere) of water. The required value of $k$ is $1{\cdot}371 \times 10^{-16}$ erg/degree. With this assigned value $k$ is a universal constant known as Boltzmann's constant.

According to this definition of the degree the ice-point lies within a few hundredths of a degree of 273·15° K., but its exact value will always be a matter of some uncertainty. This small uncertainty is of trivial importance at ordinary temperatures, but it can cause serious ambiguity when one expresses temperatures below 1° K. on the Celsius scale (commonly called the centigrade scale), which has its zero at the ice-point. Giauque* has therefore made the useful suggestion that the degree should be redefined by fixing *exactly* the ice-point. Whether this is fixed at 273·1° K. or 273·2° K., or at any intermediate value, the difference between the steam-point and the ice-point will still be 100 degrees within the present experimental uncertainty.

The average value of any extensive property per mole is equal to that per molecule multiplied by Avogadro's number $\mathsf{N} = 6{\cdot}06_4 \times 10^{23}$. When energies are expressed per mole, then $k$ has to be replaced by

$$\mathsf{N}k = R. \qquad (226, 2)$$

This quantity is called the gas constant and has a value $8{\cdot}314 \times 10^7$ ergs/deg. or 8·314 joules/deg. or 1·986 cal./deg.

**§ 227. Distribution laws in terms of the Kelvin temperature $T$.** Now that we have established the relation (224, 1) between $\vartheta$ and $T$, it is convenient to reformulate the distribution law in terms of $T$. By substituting (224, 1) into (217 ,1), we obtain

$$n_r = \frac{\varpi_r}{e^{\epsilon_r/kT}/\lambda_A \pm 1}, \qquad (227, 1)$$

with $\lambda_A$ determined by the necessary equality

$$\Sigma_r n_r = N_A. \qquad (227, 2)$$

For classical statistics ($\lambda_A \ll 1$) these relations reduce to

$$n_r = \lambda_A \varpi_r e^{\epsilon_r/kT} = N_A \frac{\varpi_r e^{-\epsilon_r/kT}}{\Sigma_r \varpi_r e^{-\epsilon_r/kT}} = N_A \frac{\varpi_r e^{-\epsilon_r/kT}}{f_A(T)}, \qquad (227, 3)$$

which could equally have been obtained by substituting (224, 1) into (218, 4) or (218, 6).

* Giauque, *Nature*, **143**. 623 (1939).

# CHAPTER III

## PERMANENT PERFECT GASES

**§ 300. Nature of perfect gases.** We may define a perfect gas as an assembly of systems between which the mutual energy of interaction is negligible. We may then regard the energy of the whole assembly as the sum of the kinetic energy of translation of the individual systems and the rotational, vibrational and electronic energies of the individual systems, referred to axes passing through the centre of mass of each system. For convenience we shall refer to the sum of the rotational, vibrational and electronic energies as the internal energy. This being so, the partition function $f(T)$ splits into two factors, one $l(T)$ for the translational energy, and the other $j(T)$ for the internal (including rotational) energy. If the rotational and vibrational motions may be treated as independent, then $j(T)$ itself factorizes into $r(T)$ for rotational energy, $q(T)$ for vibrational energy, and $e(T)$ for electronic energy. At present we are unjustifiably ignoring the nuclear structure, and treating the nucleus as a massive point. We shall correct this inaccuracy in § 315.

We shall begin by considering the translational motion and shall deduce the laws of perfect gases. Since we shall see that monatomic molecules have no variable internal energy, many of their properties are completely determined by the translational partition function $l(T)$. We shall afterwards consider the rotational and vibrational motions so as to deduce the properties of gases having diatomic and polyatomic molecules.

In Chapter II the free energy $F$ and the total energy $E$ were each expressed as the sum of contributions $F_A, F_B, \ldots$ and $E_A, E_B, \ldots$ of sets of systems $A$, $B$, .... The condition for $F$ and $E$ to be expressible in this form is the absence of any appreciable interaction between the systems $A$ and the systems $B$. This requirement is satisfied if either (1) the several sets $A$, $B$, ... are in different enclosures, or (2) the several sets are perfect gases in the same enclosure. The former condition is fulfilled when $F_A, F_B, \ldots$ and $E_A, E_B, \ldots$ denote the contributions of several homogeneous phases; in the assemblies under discussion in this chapter it is the second condition which is fulfilled.

**§ 301. Quantized translational motion.** We have already derived in Chapter II the formulae for the translational motion of an assembly of particles in an enclosure. We are interested only in the case where classical statistics is valid. If the mass of the molecules of type $A$ is $m_A$, then by

(219, 9) the translational partition function $l_A(T)$ for these molecules is

$$l_A(T) = (2\pi m_A kT)^{\frac{3}{2}} V/h^3. \qquad (301, 1)$$

Consequently by (225, 4) the free energy is

$$F = -kT\,\Sigma_A N_A\{\log l_A(T)\, j_A(T) - \log N_A + 1\}$$

$$= -kT\,\Sigma_A N_A\left\{\log \frac{(2\pi m_A kT)^{\frac{3}{2}} V}{h^3} - \log N_A + 1\right\} - kT\,\Sigma_A N_A \log j_A(T)$$

$$= -kT\,\Sigma_A N_A\left\{\log \frac{(2\pi m_A kT)^{\frac{3}{2}} V}{h^3} - \log N_A + 1\right\} + F^{(j)}, \qquad (301, 2)$$

where $F^{(j)}$ is the contribution of the internal (including rotational) degrees of freedom, and from their nature we may expect $j_A(T)$ and so $F^{(j)}$ to be independent of $V$; this will be verified when we obtain explicit formulae for $j_A(T)$ and $F^{(j)}$. If now we regard $V$ as a parameter or generalized coordinate, then the conjugate generalized force is the pressure $P$ and consequently

$$P = -\partial F/\partial V = \Sigma_A N_A kT/V. \qquad (301, 3)$$

This is the familiar equation of state for a mixture of perfect gases, and includes the laws of Boyle, Charles, Avogadro, and Dalton. For an assembly of systems of a single type (3) reduces to

$$P = NkT/V. \qquad (301, 4)$$

It is hardly necessary to discuss the field of validity of these formulae. Since actual gases are not perfect, the properties of perfect gases cannot strictly be said to be observed. They must be obtained by extrapolation to zero concentration from the actual observations at ordinary concentrations. This presents no serious difficulty and introduces little uncertainty into the results. In this chapter we shall suppose that the necessary corrections have been made. The formulae required for doing this will be given in Chapter VII. It is a commonplace that (3) is accurately the limit of the actual equation of state for all permanent gases or gas mixtures at all temperatures, except very near to the absolute zero, when Fermi-Dirac or Bose-Einstein statistics must be used. For most of the simpler gases the equation of state is already very near to its limiting form at normal pressures of the order of one atmosphere, even if the temperature is low.

We shall require to use two alternative forms of (3).

(i) If we define the partial pressure $p_A$ of systems $A$ in a gas, whether perfect or not, by

$$p_A = \frac{N_A}{\Sigma_A N_A} P, \quad \Sigma_A p_A = P, \qquad (301, 5)$$

then for a perfect gas we have according to (3)

$$p_A = N_A kT/V. \qquad (301, 6)$$

(ii) For any phase whatever the partial molecular volume $V_A$ of a system $A$ is defined thermodynamically by

$$V_A = (\partial V/\partial N_A)_{T,P}; \tag{301, 7}$$

for a perfect gas we obtain from (3)

$$V_A = kT/P. \tag{301, 8}$$

We also deduce from (2) that the total energy of the gas is

$$E = -T^2\left(\frac{\partial F/T}{\partial T}\right)_V = \Sigma_A \tfrac{3}{2} N_A kT + E^{(i)}, \tag{301, 9}$$

where $E^{(i)}$ is the energy due to the internal degrees of freedom (rotational and vibrational) and is independent of $V$ (or $P$).

The molecular energy $E_A$ of a system $A$ in any phase is defined thermodynamically by

$$E_A = (\partial E/\partial N_A)_{T,P}. \tag{301, 10}$$

When $E_A$ is correctly defined by (10), then for any kind of assembly*

$$E = \Sigma_A N_A E_A. \tag{301, 11}$$

According to (9) we thus obtain for a perfect gas

$$E_A = \tfrac{3}{2}kT + E^{(i)}, \tag{301, 12}$$

where $E^{(i)}$ is independent of $V$ (or $P$).

Incidentally as $E$ for a perfect gas is independent of $V$ (or $P$) we have

$$(\partial E/\partial N_A)_{T,V} = E_A = (\partial E/\partial N_A)_{T,P}, \tag{301, 13}$$

but it is important to remember that the equality (13) is peculiar to perfect gases, while the relations (10) and (11) are true for all homogeneous phases. In Chapter XI we shall see that for the free electrons in a metal (11) is true but not (13).

If we suppose the gas contained in a rectangular box, then, according to the discussion in § 219, the translational motion is separable into motions parallel to the three edges of the box. The translational partition function $l(T)$ may therefore be further factorized into $l_x(T)$, $l_y(T)$, $l_z(T)$ corresponding to the three directions of motion. The energies are additive, and by (219, 2) the energy levels for motion in the $x$-direction are

$$\epsilon_r = r^2h^2/8m_A a^2, \tag{301, 14}$$

where $a$ is the length of the box in the $x$-direction and the quantum number $r$ can take any positive (not zero) integral values. So far as concerns motion in this one direction, the states are completely described by the single

* See *M.T.* p. 31.

quantum number $r$ and so each state has the weight unity. The partition function $l_x(T)$ for motion in the $x$-direction is

$$l_x(T) = \Sigma_r e^{-r^2h^2/8m_Aa^2kT} = \int_0^\infty e^{-r^2h^2/8m_Aa^2kT}dr = (2\pi m_A kT)^{\frac{1}{2}} a/h. \quad (301, 15)$$

In replacing the sum by an integral we have assumed that

$$h^2/(8m_A a^2) \ll 1, \quad (301, 16)$$

which we have already verified to be true for all ordinary gases in § 219. The number $n_r$ of molecules in the state $r$ is

$$n_r = e^{-\epsilon_r/kT}/l_x(T)$$

$$= \frac{h}{(2\pi m_A kT)^{\frac{1}{2}} a} e^{-r^2h^2/8m_Aa^2kT}. \quad (301, 17)$$

The quantum number $r$ has the simple physical meaning that in the state $r$ the square of the momentum in the $x$-direction is given by

$$|p_x|^2 = r^2h^2/4a^2, \quad (301, 18)$$

or

$$r = 2a\,|p_x|/h. \quad (301, 19)$$

We may therefore with sufficient accuracy say that the number of translational levels in the $x$-direction in which the magnitude of the momentum lies between $|p_x|$ and $|p_x| + d|p_x|$ is $2d|p_x|a/h$. At the same time the energy $\epsilon_r$ may be expressed in the form

$$\epsilon_r = \tfrac{1}{2}\,|p_x|^2/m_A. \quad (301, 20)$$

The average number $\overline{n(d|p_x|)}$ of molecules with momenta of magnitudes in the range $|p_x|$ to $|p_x| + d|p_x|$ is therefore

$$\overline{n(d|p_x|)} = \frac{N_A e^{-\frac{1}{2}|p_x|^2/m_AkT}(2a/h)\,d|p_x|}{\int_0^\infty e^{-\frac{1}{2}|p_x|^2/m_AkT}(2a/h)\,d|p_x|}, \quad (301, 21)$$

the limits of integration in the denominator being 0 to $\infty$ because $|p_x|$ by definition must be positive. When we evaluate the integral, (21) becomes

$$\overline{n(d|p_x|)} = \frac{N_A}{(2\pi m_A kT)^{\frac{1}{2}}} e^{-\frac{1}{2}|p_x|^2/m_AkT}\,2d|p_x|. \quad (301, 22)$$

This is the quantal equivalent of Maxwell's law. The factor 2 preceding $d|p_x|$ occurs because classically, corresponding to each interval $p_x$ to $p_x + dp_x$, there is a corresponding range of opposite direction $-p_x$ to $-(p_x + dp_x)$, whereas quantally we may only describe a molecule as moving back and forth with a constant $|p_x|$, but with $p_x$ alternating in sign.

**§ 302. Classical derivation of Maxwell's law.** Formula (301, 22) derived strictly from quantal considerations is equivalent to Maxwell's distribution law. It is, however, hardly satisfactory to be content with only such a sophisticated derivation of these familiar classical laws. Having shown that quantal restrictions on accessibility are usually irrelevant for systems in the gaseous phase of an assembly, and that the spacing of the characteristic energies is very small compared with $kT$ even down to $1^\circ$ K., we are justified in deducing Maxwell's distribution law and similar classical theorems in a classical manner *ab initio*. Such deductions are still of value in providing physical insight into the formulae, and we now proceed to give them. For simplicity we shall suppose that the assembly consists of $N$ particles, of mass $m$ moving freely in a volume $V$, whose energy is solely kinetic energy of translation. The whole discussion applies equally well to any number of types of systems. Internal (rotational and vibrational) degrees of freedom of molecules can be taken care of by separate partition functions.

The phase space for a free atom is specified by the six coordinates $x$, $y$, $z$, $p_x$, $p_y$, $p_z$, and is divided up into small cells of extension

$$d\omega_r = (dx\,dy\,dz\,dp_x\,dp_y\,dp_z)_r. \qquad (302, 1)$$

According to the principles of §§ 104, 202 the corresponding weight $\delta_r$ is given by

$$\delta_r = d\omega_r/h^3. \qquad (302, 2)$$

To take account of the confinement of the systems to the volume $V$, we start with the systems in an external field of force of potential energy $u$, which may finally be reduced to the local boundary field of the walls. Then there is an energy $\epsilon_r$ associated with the $r$th cell given by

$$\epsilon_r = \tfrac{1}{2}(p_x^2+p_y^2+p_z^2)/m + u_r, \qquad (302, 3)$$

where $u_r$ is a function of $x$, $y$, $z$ but is independent of $p_x$, $p_y$, $p_z$. We may then class together all states of a system represented by a point in the element $d\omega_r$ of phase space as a single degenerate state of energy $\epsilon_r$ given by (3), and weight $\delta_r$ given by (2). The partition function $l(T)$ becomes

$$l(T) = \Sigma_r\, \delta_r e^{-\epsilon_r/kT}, \qquad (302, 4)$$

which can be expressed as the integral

$$l(T) = \frac{1}{h^3}\int_{-\infty}^{+\infty} dx \int_{-\infty}^{+\infty} dy \int_{\infty}^{+\infty} dz \int_{-\infty}^{+\infty} dp_x \int_{-\infty}^{+\infty} dp_y \int_{-\infty}^{+\infty} dp_z\, e^{-[\frac{1}{2}(p_x^2+p_y^2+p_z^2)/m+u]/kT}. \qquad (302, 5)$$

For an assembly confined to a volume $V$ we can represent the effect of the walls by setting

$$\begin{aligned} u &= 0 \quad (x, y, z \text{ inside } V), \\ u &= \infty \quad (x, y, z \text{ outside } V). \end{aligned} \qquad (302, 6)$$

If then we define the element of volume $dV$ by

$$dV = dxdydz, \tag{302, 7}$$

we have

$$l(T) = \frac{1}{h^3}\int_V dV \int_{-\infty}^{+\infty} dp_x \int_{-\infty}^{+\infty} dp_y \int_{-\infty}^{+\infty} dp_z \, e^{-\frac{1}{2}(p_x^2+p_y^2+p_z^2)/mkT}, \tag{302, 8}$$

where the integration of $dV$ is just over the prescribed volume $V$. We can also perform the other integrations and obtain

$$l(T) = (2\pi mkT)^{\frac{3}{2}} \, V/h^3, \tag{302, 9}$$

in agreement with (301, 1). The average number $\overline{n(d\omega)}$ of molecules whose state is represented by a point in the element $d\omega = dxdydzdp_xdp_ydp_z$ of phase space is given by

$$\overline{n(d\omega)} = (N/V)(2\pi mkT)^{-\frac{3}{2}} \, e^{-\frac{1}{2}(p_x^2+p_y^2+p_z^2)/mkT} \, dxdydzdp_xdp_ydp_z, \tag{302, 10}$$

which is Maxwell's law.

§ 303. **Special cases.** By performing the $p_x$, $p_y$, $p_z$ integrations we obtain the physically obvious result that the average number $n(dV)$, of molecules in the element of volume $dV$, is given by

$$n(dV) = NdV/V, \tag{303, 1}$$

which means that in an enclosure of uniform potential the molecules are distributed uniformly. Similarly by performing the $x$, $y$, $z$ integrations in (302, 10) we obtain for the average number of particles with momenta in the ranges $p_x$, $p_x + dp_x$; $p_y$, $p_y + dp_y$; $p_z$, $p_z + dp_z$,

$$\overline{n}(dp_x, dp_y, dp_z) = N(2\pi mkT)^{-\frac{3}{2}} \, e^{-\frac{1}{2}(p_x^2+p_y^2+p_z^2)/mkT} \, dp_xdp_ydp_z. \tag{303, 2}$$

This can be expressed in an alternative form for the average number of molecules with *velocity* components in the ranges $u$, $u+du$; $v$, $v+dv$; $w$, $w+dw$,

$$\overline{n}(du, dv, dw) = N(m/2\pi kT)^{\frac{3}{2}} \, e^{-\frac{1}{2}m(u^2+v^2+w^2)/kT} \, dudvdw, \tag{303, 3}$$

which is Maxwell's distribution law for velocities. It is often convenient to describe the velocity distribution by means of a distribution function $g(u, v, w)$ such that $g(u, v, w)\,dudvdw$ is equal to the fraction of all the molecules whose velocity components lie in the ranges $u$, $u+du$; $v$, $v+dv$; $w$, $w+dw$. Maxwell's law (3) can then be expressed in the form

$$g(u, v, w) = (m/2\pi kT)^{\frac{3}{2}} \, e^{-\frac{1}{2}m(u^2+v^2+w^2)/kT}. \tag{303, 4}$$

For many purposes one is interested only in the distribution of the velocity component in a single direction, say the $x$-direction. The number $\overline{n(du)}$ of molecules with velocity component in the $x$-direction between $u$

and $u+du$ is obtained from (4) by integration over $v$ and $w$ from $-\infty$ to $+\infty$. We thus find

$$\overline{n(du)} = N(m/2\pi kT)^{\frac{1}{2}} e^{-\frac{1}{2}mu^2/kT} du, \qquad (303, 5)$$

or, if we denote by $g(u)du$ the fraction of all molecules with velocity component in the $x$-direction between $u$ and $u+du$, then the distribution function $g(u)$ is given by

$$g(u) = (m/2\pi kT)^{\frac{1}{2}} e^{-\frac{1}{2}mu^2/kT}. \qquad (303, 6)$$

Occasionally one is more interested in the resultant velocity $c$ than in the components $u$, $v$, $w$ along specified axes. We then transform (3) to spherical polar coordinates $c$, $\theta$, $\phi$. We obtain for the average number of molecules with resultant velocity in the range $c$, $c+dc$; $\theta$, $\theta+d\theta$; $\phi$, $\phi+d\phi$

$$\overline{n(dc, d\theta, d\phi)} = N(m/2\pi kT)^{\frac{3}{2}} e^{-\frac{1}{2}mc^2/kT} c^2 \sin\theta\, dc\, d\theta\, d\phi. \qquad (303, 7)$$

We can now integrate with respect to $\theta$ from 0 to $\pi$ and with respect to $\phi$ from 0 to $2\pi$, and so obtain for the total number of molecules with resultant velocity in the range $c$, $c+dc$

$$\overline{n(dc)} = 4\pi N(m/2\pi kT)^{\frac{3}{2}} e^{-\frac{1}{2}mc^2/kT} c^2\, dc. \qquad (303, 8)$$

These velocity distribution laws enable us to calculate the number of events, such as collisions of a definite type, which occur per unit time and per unit volume of the gas or per unit area of the surface of a wall. Results of this type are of importance for adsorption, thermionics and chemical kinetics; they will be derived and used in later chapters.

**§ 304. Distribution in an external field.** To determine the average distribution of systems in an external field according to quantum theory, we should solve Schrödinger's equation

$$\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right)\psi + \frac{8\pi^2 m}{h^2}(\epsilon - u)\psi = 0, \qquad (304, 1)$$

where $u$ is the potential energy expressed as a function of $x$, $y$, $z$. Having determined the energy levels and weights of the various states we should then apply the general formulae. This can be carried out explicitly only if $u(x, y, z)$ separates into $u_1(x)+u_2(y)+u_3(z)$ and even then the treatment is complicated.* However, knowing that, under all realizable conditions for a gas, the separation of the energy levels will be small compared with $kT$, we can avoid this difficulty by making use of the limiting principle and applying a classical treatment. Using the classical form (302, 5) of $l(T)$ and the formula (227, 3) it follows at once that the average number $\overline{n(d\omega_r)}$ of systems, whose

* *S M* § 2·71

coordinates and momenta lie in the element $d\omega_r$ of phase space, is given by

$$\overline{n(d\omega_r)} = N\frac{e^{-[\frac{1}{2}(p_x^2+p_y^2+p_z^2)/m+u]/kT}\,(dx\,dy\,dz\,dp_x\,dp_y\,dp_z)_r}{\int_{-\infty}^{+\infty}dx\int_{-\infty}^{+\infty}dy\int_{-\infty}^{+\infty}dz\int_{-\infty}^{+\infty}dp_x\int_{-\infty}^{+\infty}dp_y\int_{-\infty}^{+\infty}dp_z\,e^{-[\frac{1}{2}(p_x^2+p_y^2+p_z^2)/m+u]/kT}}. \tag{304, 2}$$

It is clear that we can integrate (2) over $x, y, z$ or over $p_x, p_y, p_z$ separately. If we integrate over $x, y, z$ we obtain for the average number $\overline{n(dp_x, dp_y, dp_z)}$ of systems with momenta lying in the ranges $p_x$, $p_x+dp_x$; $p_y$, $p_y+dp_y$; $p_z$, $p_z+dp_z$ the formula

$$\overline{n(dp_x, dp_y, dp_z)} = N(2\pi mkT)^{-\frac{3}{2}}\,e^{-\frac{1}{2}(p_x^2+p_y^2+p_z^2)/mkT}\,dp_x\,dp_y\,dp_z, \tag{304, 3}$$

identical with (303, 2). This important result means that Maxwell's distribution law for the momenta (or velocities) is not affected by the presence of an external field.

If on the other hand we perform the integrations over $p_x$, $p_y$, $p_z$ in (2) we obtain for the average number $\overline{n(dV)}$ of systems in the element of volume $dV = dx.dy.dz$

$$\overline{n(dV)} = N\frac{e^{-u/kT}\,dx\,dy\,dz}{\int_{-\infty}^{+\infty}dx\int_{-\infty}^{+\infty}dy\int_{-\infty}^{+\infty}dz\,e^{-u/kT}}. \tag{304, 4}$$

By applying this to two different volume elements $dV_1$, $dV_2$, where the potential energy of the systems is $u_1$, $u_2$, we obtain

$$\frac{\overline{n(dV_1)}}{\overline{n(dV_2)}} = \frac{e^{-u_1/kT}\,dV_1}{e^{-u_2/kT}\,dV_2}, \tag{304, 5}$$

or, introducing the concentration $C$, defined as the number of systems per unit volume, we have

$$C_1 : C_2 = e^{-u_1/kT} : e^{-u_2/kT}. \tag{304, 6}$$

This formula expresses Boltzmann's law for the distribution of systems in an external field.

**§ 305. Sedimentation. Perrin's determination of Avogadro's number.** Boltzmann's formula (304, 6) forms the basis of one of Perrin's* determinations of Avogadro's number. For a uniform gravitational field of intensity $g$, the distribution law becomes

$$C_1 : C_2 = e^{-mgh/kT}, \tag{305, 1}$$

where $m$ denotes the mass of the particle, and $h$ the difference of height between the two volume elements considered. Perrin's experiments were made not on a gas but on a colloidal suspension of mastic particles in a liquid medium. We have therefore to replace $m$ by an effective mass $V(\rho-\rho_0)$,

* Perrin, *La Théorié du Rayonnement et les Quanta*, p. 183 (Gauthier-Villars, 1911).

where $V$ denotes the volume of a particle, $\rho$ its density and $\rho_0$ the density of the surrounding liquid. We have then, instead of (1),

$$C_1 : C_2 = e^{-V(\rho-\rho_0)gh/kT}. \qquad (305, 2)$$

Perrin measured directly the ratio $C_1 : C_2$, the height $h$, and the volume $V$ of the particles. Thus, knowing $T$ and $g$, he obtained an absolute value for $k$. By comparing this value with the experimental value of the gas constant $R$ for a mole (gram-molecule) of a perfect gas obtained from the equation of state, he calculated Avogadro's number from the relation

$$\mathsf{N} = R/k. \qquad (305, 3)$$

This was one of the earliest determinations of **N** by a method which is in principle completely accurate. The experimental difficulties of preparing mastic particles of uniform size and of measuring their size and density limits the accuracy of the method. Even so Perrin obtained a value for **N** differing by only about 15 % from the value $0{\cdot}606 \times 10^{24}$ since determined by other methods, which are experimentally more accurate.

**§ 306. Classical statistics and classical mechanics.** We have already seen in § 218 that instead of using one kind of statistics for assemblies of localized systems, another kind (Fermi-Dirac) for assemblies with eigen functions antisymmetrical in all identical systems, and a third kind (Bose-Einstein) for assemblies with eigen functions symmetrical in all identical systems, we may almost always use one and the same kind of statistical formulae for all assemblies. This universal treatment of assemblies of all three types is called *classical statistics*. The condition for its applicability is, roughly speaking, that the number of available states of not too great energy is very large compared with the number of systems in the assembly. This condition is fulfilled by all assemblies commonly dealt with, except that of free electrons in a metal.

The formulae of *classical statistics* are still quantal formulae from a dynamic point of view, inasmuch as they refer explicitly to the individual quantum states of the systems. By *classical dynamics*, on the other hand, we mean a dynamic treatment of energy, momentum and the like, in which no reference is made to quantization. Generally speaking *classical dynamics* is an adequate approximation, as long as the separations between the quantal energy levels are small compared with all other energy quantities relevant to the particular problem. In statistical mechanics the most important and often the only relevant such energy quantity is $kT$, and so we may as a general rule ignore quantum theory when we know that the separation of energy levels is small compared with $kT$. This is just the situation, as we have seen, in the translational motion of the molecules of a gas.

We shall find it convenient to use the expression *classical degree of freedom* to denote any degree of freedom, such as the translational degrees of freedom of gaseous molecules, to which we may with sufficient accuracy apply classical dynamics.

**§ 307. Classical and unexcited degrees of freedom.** For any *classical* degree of freedom the partition function is given according to the limiting process by replacing the sum by an integral. Thus for a single classical degree of freedom

$$f(T) = \frac{1}{h}\int e^{-\epsilon/kT}\,dx\,dp_x. \tag{307, 1}$$

As we have seen, the condition for a particular degree of freedom to be *classical* is that all the separations between successive energy levels are much smaller than $kT$. The opposite extreme case occurs when

$$\epsilon_1 - \epsilon_0 \gg kT, \tag{307, 2}$$

where $\epsilon_0$, $\epsilon_1$ denote the energies of the lowest and next to lowest energy levels. In this case the partition function reduces to its first term

$$f(T) = \varpi_0 e^{-\epsilon_0/kT}, \tag{307, 3}$$

and we refer to such a degree of freedom as an *unexcited degree of freedom*. It will usually be convenient to define the zero of energy for each degree of freedom as that of the lowest state, so that

$$\epsilon_0 = 0, \tag{307, 4}$$

and (3) then simplifies to

$$f(T) = \varpi_0. \tag{307, 5}$$

**§ 308. Electronic degrees of freedom.** One of the factors of $j(T)$ the partition function for internal energy is that due to the electronic degrees of freedom, of which there are four (three translational and one of spin) for each electron. Under ordinary conditions the separation between the lowest energy level $\epsilon_0$ and the next lowest $\epsilon_1$ of most, but not all, normal molecules greatly exceeds $kT$. The electronic degrees of freedom are then unexcited, and the electronic partition function $e(T)$ reduced to its first term $\upsilon_0 e^{-\epsilon_0/kT}$, where $\upsilon_r$ denotes the weight of the $r$th electronic level. If we choose as zero the normal energy level of the molecule, the electronic partition function becomes simply $\upsilon_0$. We have therefore merely to insert the factor $\upsilon_0$ into the partition function, and may otherwise ignore the electronic degrees of freedom. In the rather exceptional case where the second electronic level may not be ignored, we have merely to substitute $\upsilon_0 + \upsilon_1 e^{-\epsilon_1/kT}$ for $\upsilon_0$; this is the case for NO. We shall postpone a discussion of the values of $\upsilon_0$ to Chapter v, where the values for various molecules will be enumerated.

**§ 309. Heat capacities of perfect gases.** According to (301, 12) the energy per molecule of a perfect gas of one component is of the form

$$E = \tfrac{3}{2}kT + E^{(j)}, \tag{309, 1}$$

where $E^{(j)}$ is by its nature independent of the volume (or pressure).

By definition $C_V$, the molecular heat capacity at constant volume, is given by

$$C_V = (\partial E/\partial T)_V, \tag{309, 2}$$

and therefore by (1)

$$C_V = \tfrac{3}{2}k + dE^{(j)}/dT. \tag{309, 3}$$

Similarly by the definition of $C_P$, the molecular heat capacity at constant pressure, we have

$$C_P = \left(\frac{\partial[E+PV]}{dT}\right)_P = \left(\frac{\partial E}{\partial T}\right)_P + P\left(\frac{\partial V}{\partial T}\right)_P. \tag{309, 4}$$

Since for a perfect gas $E$ does not depend on $P$ or $V$, we have, using (301, 8)

$$C_P = C_V + P\left(\frac{\partial V}{\partial T}\right)_P = \tfrac{3}{2}k + \frac{dE^{(j)}}{dT} + k. \tag{309, 5}$$

Comparing (3) and (5) we see that

$$C_P - C_V = k. \tag{309, 6}$$

The relation (6) is well known to be obeyed accurately by gases, so that the values of $C_V$, $C_P$ are both determined when we know either separately, or their ratio $C_P/C_V$, usually denoted by $\gamma$.

In order to progress further we have to know the form of $E^{(j)}$ and this requires a discussion of the internal degrees of freedom. For this purpose it is most convenient to deal separately with gases having monatomic, diatomic and polyatomic molecules.

**§ 310. Monatomic molecules.** Apart from the electronic degrees of freedom which may be assumed unexcited, a monatomic molecule has no internal degrees of freedon.* The internal partition function $j(T)$ thus reduces to $\upsilon_0$, when the lowest electronic level is chosen as energy zero. The translational partition function is given by (302, 9). Hence for the resultant partition function of a monatomic molecule we have

$$f(T) = \frac{(2\pi m kT)^{\frac{3}{2}} V}{h^3} \upsilon_0. \tag{310, 1}$$

According to (225, 4) the free energy of an assembly of $N$ molecules is

* This statement is not strictly true and will require to be revised later when we consider nuclear spin.

therefore given by

$$F = -NkT\log\left\{\frac{(2\pi mkT)^{\frac{3}{2}}Vv_0}{h^3}\right\} + NkT(\log N - 1)$$

$$= NkT\left\{\log\frac{N}{V} - 1\right\} - \tfrac{3}{2}NkT\log T - NkT\log\left\{\frac{(2\pi mk)^{\frac{3}{2}}v_0}{h^3}\right\}. \quad (310, 2)$$

For the energy $E$ we have

$$E = -T^2\left(\frac{\partial F/T}{\partial T}\right)_{V,N} = \tfrac{3}{2}NkT. \quad (310, 3)$$

For the pressure $P$ we have

$$P = -\left(\frac{\partial F}{\partial V}\right)_{T,N} = \frac{NkT}{V}. \quad (310, 4)$$

For the partial potential $\mu$ we have

$$\mu = \left(\frac{\partial F}{\partial N}\right)_{T,V} = kT\log\frac{N}{V} - \tfrac{3}{2}kT\log T - kT\log\left\{\frac{(2\pi mk)^{\frac{3}{2}}v_0}{h^3}\right\}, \quad (310, 5)$$

or using (301, 6)

$$\mu = kT\log p - \tfrac{5}{2}kT\log T - kT\log\left\{\frac{(2\pi m)^{\frac{3}{2}}k^{\frac{5}{2}}v_0}{h^3}\right\}. \quad (310, 6)$$

**§ 311. Heat capacities of monatomic molecules.** According to (310, 3) we have for the energy per molecule of a monatomic gas, referred to its lowest state as energy zero,

$$E = \tfrac{3}{2}kT. \quad (311, 1)$$

According to the formulae of § 309, we have therefore

$$C_V = \tfrac{3}{2}k, \quad (311, 2)$$

$$C_P = \tfrac{5}{2}k, \quad (311, 3)$$

$$\gamma = C_P/C_V = \tfrac{5}{3}. \quad (311, 4)$$

Of the three quantities, $C_V$, $C_P$ and $\gamma$, the first is extremely difficult to measure and it is usual to determine either $C_P$ by a flow method or $\gamma$ by measuring the velocity of sound. The experimental data, extrapolated to zero pressure, are compared with theory in Table 1. The agreement is good.

We have assumed that the electronic degrees of freedom are unexcited and we should perhaps verify this. For the species ordinarily capable of existing as atoms in the free state, the energy $\epsilon_1$ required for excitation from the normal to the first excited state varies from 4 to 20 electron-volts, while $kT$ in electron-volts has the value $8{\cdot}60 \times 10^{-5}\,T$. Thus $\epsilon_1/kT$ is at least $\frac{1}{2} \times 10^5/T$, and so in the electronic partition function the first, and *a fortiori* all subsequent, excited terms are negligible compared with the normal term, unless $T$ is at least 10,000° K.

TABLE 1

*Values of $C_P$ and of $\gamma$ for monatomic gases*

Theoretical values: $C_P/k = 2\cdot50$; $\gamma = C_P/C_V = 1\cdot667$

| Substance | Determinations of $C_P$ | | | Determinations of $\gamma$ | | |
|---|---|---|---|---|---|---|
| | Temp. °K. | $C_P/k$ | Observers | Temp. °K. | $\gamma$ | Observers |
| He | 291 | 2·51 | S.H. | — | — | — |
| Ne | — | — | — | 292 | 1·64 | Ramsay |
| A | 288 | 2·54 | Heuse | 284 | 1·66 | R.R. |
| Kr | — | — | — | 292 | 1·69 | Ramsay |
| Xe | — | — | — | 292 | 1·67 | Ramsay |
| Na | — | — | — | 750– 920 | 1·68 | Robitzsch |
| K | — | — | — | 660–1000 | 1·64 | Robitzsch |
| Hg | — | — | — | 548– 629 | 1·666 | K.W. |

*References to Table 1*

S.H.: Scheel and Heuse, *Ann. d. Phys.* **40**, 473 (1913).
Heuse, *Ann. d. Phys.* **59**, 86 (1919).
Ramsay, *Proc. Roy. Soc.* A, **86**, 100 (1912).
K.W.: Kundt and Warburg, *Ann. d. Phys.* **157**, 353 (1876).
Robitzsch, *Ann. d. Phys.* **38**, 1027 (1912).
R.R.; Rayleigh and Ramsay, *Phil. Trans. Roy. Soc.* **186**, 228 (1895).

Many free atoms, for example thallium, not commonly experimented with as vapours, possess however a normal state, which is the lowest state of a multiplet. For such atoms the smallest excitation energy may be comparatively small, and the internal energy may make an important contribution to the heat capacity. Though such cases are not yet of practical importance we shall assemble the formulae in § 324, as they are of general utility.

**§ 312. Diatomic gases at moderate temperatures.** In addition to the types of motion and energy content which they share with free atoms, diatomic molecules possess further types of motion. The atomic nuclei can rotate about their centre of mass, to a first approximation like a rigid body, and can vibrate along the line joining them, to a first approximation like a simple harmonic oscillator. If the molecule is nearly rigid, so that the frequency of these vibrations is high, the rotations and vibrations are nearly independent of each other. Moreover, at fairly low temperatures the nuclear vibrations will be unexcited, and the whole extra motion reduces to the rotations of a rigid body. The non-vibrating molecule must indeed stretch under the centrifugal forces, but for stiff molecules of high vibrational frequency this effect will be small for moderate rotations—that is, at low temperatures.

Just as for monatomic molecules the electronic motions are usually completely unexcited, and the electronic partition function reduces to its first term $\varpi_0 e^{-\epsilon_0/kT}$, or, if the energy zero is chosen as the normal state, simply $\varpi_0$. It may, however, happen that there is another electronic state low enough to contribute appreciably to the partition function, in which case we have to replace $\varpi_0$ by $\varpi_0 + \varpi_1 e^{-\epsilon_1/kT}$. Important examples actually occur among simple permanent gases (e.g. NO) and are discussed in § 325. To account for the properties of diatomic gases we therefore chiefly need to consider in some detail the rotational partition functions.

**§ 313. Rotational degrees of freedom.** Apart from the electronic motions (and nuclear spin discussed in § 315) a diatomic molecule can have no angular momentum about the axis through the two nuclei. Thus the correct model for its rotational motion is the rigid rotator without axial spin, described in § 212. We have then the rotational partition function

$$r(T) = \sum_{j=0}^{\infty} (2j+1)\, e^{-j(j+1)\Theta_r/T}, \tag{313, 1}$$

where

$$\Theta_r = h^2/8\pi^2 A k. \tag{313, 2}$$

When $\Theta_r \ll T$, as is the case at ordinary temperatures for all diatomic molecules, and even at low temperatures for diatomic molecules not containing a hydrogen atom, we may use Mulholland's approximate formula (212, 7)

$$r(T) = \frac{T}{\Theta_r}\left\{1 + \frac{1}{3}\frac{\Theta_r}{T} + \frac{1}{15}\frac{\Theta_r^2}{T^2} + O\left(\frac{\Theta_r}{T}\right)^3\right\}, \tag{313, 3}$$

from which we derive by (301, 2) for $F^{\text{rot}}$, the contribution of the rotational degrees of freedom to the free energy,

$$F^{\text{rot}} = -NkT \log r(T) = NkT\left\{\log\frac{\Theta_r}{T} - \frac{1}{3}\frac{\Theta_r}{T} - \frac{1}{90}\frac{\Theta_r^2}{T^2} + O\left(\frac{\Theta_r}{T}\right)^3\right\}, \tag{313, 4}$$

and for $E^{\text{rot}}$ the contribution of the rotational degrees of freedom to the total energy

$$E^{\text{rot}} = -T^2\frac{\partial F^{\text{rot}}/T}{\partial T} = NkT\left\{1 - \frac{1}{3}\frac{\Theta_r}{T} - \frac{1}{45}\frac{\Theta_r^2}{T^2} + O\left(\frac{\Theta_r}{T}\right)^3\right\}. \tag{313, 5}$$

Finally for $C^{\text{rot}}$, the contribution of the rotational degrees of freedom to the molecular heat capacity, we obtain by differentiating (5) with respect to $T$ and dividing by $N$,

$$C^{\text{rot}} = k\left\{1 + \frac{1}{45}\frac{\Theta_r^2}{T^2} + O\left(\frac{\Theta_r}{T}\right)^3\right\} = k\left\{1 + \frac{1}{45}\left(\frac{h^2}{8\pi^2 A kT}\right)^2 + O\left(\frac{h^2}{AkT}\right)^3\right\}. \tag{313, 6}$$

**§ 314. Classical treatment of rotation of diatomic molecules.** We have seen that, at ordinary temperatures, $\Theta_r \ll T$ at least for all molecules not containing hydrogen. This means that the rotational degrees of freedom are classical, and we may therefore make use of the limiting principle to replace the partition function by the corresponding phase integral. The classical formulae for the dynamics of a rigid rotator without axial spin are given in § 204. Consequently the phase integral which gives the limiting form of the partition function $r(T)$ is

$$\frac{1}{h^2}\int_0^{2\pi} d\phi \int_0^{\pi} d\theta \int_{-\infty}^{+\infty} dp_\phi \int_{-\infty}^{+\infty} dp_\theta \, e^{-\frac{1}{2}(p_\theta^2+p_\phi^2/\sin^2\theta)/AkT} = \frac{8\pi^2 A kT}{h^2}, \quad (314, 1)$$

in agreement with the leading term of (313, 3) for $\Theta_r \ll T$.

**§ 315. Nuclear symmetry.** In evaluating the integral (314, 1) we paid no attention to symmetry with respect to the two nuclei. In molecules with two different nuclei (heteronuclear molecules), there is no need to do so. In the case of molecules containing two identical nuclei (homonuclear molecules) on the other hand, each half rotation brings the molecule back to a position indistinguishable from that from which it started. If then we use the phase integral (314, 1) with the limits there given, we are counting twice over every physically distinguishable orientation. The question arises whether one should not therefore correct for this by dividing the result by 2. Actually this procedure leads to correct results. Hence according to the limiting principle we must expect a similar correction to arise in a strict quantal treatment. We shall now consider how this arises, and shall in fact show that it comes from the necessity of distinguishing between eigen functions symmetrical and antisymmetrical in the nuclei.

Up to the present we have assumed that the motion of a molecule can be decomposed into translational motion of the centre of mass, rotational motion, vibrational motion and electronic motion, with a corresponding factorization of the eigen function. We have tacitly ignored any possible nuclear structure. Strictly we must allow for this by introducing nuclear factors, but the only relevant factor at terrestrial temperatures is the factor due to the spin of the lowest nuclear state, all other states having energies exceeding that of the lowest state by amounts which are exceedingly large compared with $kT$. Owing to this spin, however, there will be orientational quantization in an external magnetic field, with an eigen function for each such orientation. In the absence of an external field these orientated states become indistinguishable, but their number $\rho$ remains unaltered, and the nucleus is therefore usefully described as being in a state of spin weight $\rho$.

Let us first consider a heteronuclear diatomic molecule made up of a nucleus $a$ with $\rho_a$ eigen functions $\psi_1, \psi_2, \ldots, \psi_\rho$ and a nucleus $b$ with $\rho_b$

eigen functions $\psi'_1, \psi'_2, \ldots, \psi'_{\rho_b}$. Then for the molecule we have nuclear eigen functions of the type $\psi_r(a)\,\psi'_s(b)$. Thus the consideration of nuclear orientations introduces into the partition function of the molecule the extra weight factor $\rho_a \rho_b$. Now consider by contrast a homonuclear diatomic molecule made up of two identical nuclei $a$ and $b$ each having $\rho$ orientational eigen functions $\psi_1, \psi_2, \ldots, \psi_\rho$. When the two nuclei form part of a single system, such as a diatomic molecule, we can obtain nuclear spin eigen functions for the system by combination of these two sets for the single nuclei. In particular we can form $\frac{1}{2}\rho(\rho-1)$, of the type $\psi_r(a)\,\psi_s(b) - \psi_s(a)\,\psi_r(b)$, antisymmetrical in the nuclei; we can similarly form $\frac{1}{2}\rho(\rho-1)$, of the type $\psi_r(a)\,\psi_s(b) + \psi_s(a)\,\psi_r(b)$, symmetrical in the nuclei, and also $\rho$ of the type $\psi_r(a)\,\psi_r(b)$, also symmetrical in the nuclei. Thus in all we can form $\frac{1}{2}\rho(\rho-1)$ antisymmetrical and $\frac{1}{2}\rho(\rho+1)$ symmetrical eigen functions for the nuclear spins of the molecule. It will be noticed that the sum of the number of antisymmetrical and symmetrical eigen functions is $\rho^2$, the same as the number of functions for a heteronuclear molecule, containing two nuclei with equal $\rho$ values.

We have next to consider the symmetry properties with respect to the nuclei of the eigen functions for the translations, vibrations and rotations of the molecule. The translational motion, being that of the centre of mass of the molecule, is independent of the relative positions of the nuclei; the eigen function does not contain the coordinates of the nuclei, and so is symmetrical in the nuclei. The vibrational eigen function is a function of the distance apart of the two nuclei. Since this distance is unaffected by an interchange of the two nuclei, the vibrational eigen function is also symmetrical in the two nuclei. The rotational eigen functions are the spherical harmonics. Those with $j = 0, 2, 4, 6, \ldots$ are symmetrical in the nuclei, those with $j = 1, 3, 5, \ldots$ are antisymmetrical in the nuclei.

Now for any given type of nuclei only those states are accessible which are antisymmetrical in the nuclei, or only those which are symmetrical. So far as is known the antisymmetrical states occur for nuclei with odd mass numbers, and the symmetrical for those with even mass numbers. If nuclei may be regarded as composed of protons and neutrons only, this conforms to the rule that the eigen function of every accessible state is antisymmetrical in electrons, in protons, and in neutrons.

Let us now consider the application of these considerations to diatomic molecules. If the molecule is heteronuclear, we have already seen that consideration of nuclear spin merely introduces an extra weight factor $\rho_a \rho_b$. For homonuclear molecules the situation is the following. If the nuclei are of odd mass number, then to obtain resultant eigen functions antisymmetrical in the nuclei, the even rotational eigen

functions ($j = 0, 2, \ldots$), being symmetrical in the nuclei, have to be combined with one of the $\frac{1}{2}\rho(\rho-1)$ antisymmetrical nuclear functions, and the odd rotational functions ($j = 1, 3, \ldots$) have to be combined with one of the $\frac{1}{2}\rho(\rho+1)$ symmetrical nuclear functions. Thus the even rotational states have an extra weight factor $\frac{1}{2}\rho(\rho-1)$ and the odd rotational states an extra factor $\frac{1}{2}\rho(\rho+1)$. If the mass number is even, then, to obtain resultant eigen functions symmetrical in the nuclei, the rotational eigen functions have to be combined with the nuclear eigen functions in the reverse manner. The result is that the even rotational states have an extra weight factor $\frac{1}{2}\rho(\rho+1)$, and the odd rotational states have an extra factor $\frac{1}{2}\rho(\rho-1)$. We thus obtain the following partition functions $r_n(T)$ for the combined rotations and nuclear orientations.

*Heteronuclear:*

$$r_n(T) = \rho_a \rho_b \sum_{j=0}^{\infty} (2j+1)\, e^{-j(j+1)\Theta_r/T}. \tag{315, 1}$$

*Homonuclear, odd mass numbers:*

$$r_n(T) = \tfrac{1}{2}\rho(\rho-1) \sum_{j=0,2,\ldots}^{\infty} (2j+1)\, e^{-j(j+1)\Theta_r/T} + \tfrac{1}{2}\rho(\rho+1) \sum_{j=1,3,\ldots}^{\infty} (2j+1)\, e^{-j(j+1)\Theta_r/T}. \tag{315, 2}$$

*Homonuclear, even mass numbers:*

$$r_n(T) = \tfrac{1}{2}\rho(\rho+1) \sum_{j=0,2,\ldots}^{\infty} (2j+1)\, e^{-j(j+1)\Theta_r/T} + \tfrac{1}{2}\rho(\rho-1) \sum_{j=1,3,\ldots}^{\infty} (2j+1)\, e^{-j(j+1)\Theta_r/T}. \tag{315, 3}$$

In the simplest case of nuclei without spin, $\rho = 1$, and we notice that the requirements of nuclear symmetry result in the complete disappearance of alternate rotational states of a homonuclear molecule. This has been completely verified spectroscopically for the molecules $He_2$, $^{16}O_2$.

We shall return shortly to a detailed discussion of the applicability of (2) and (3) at low temperatures. But at ordinary temperatures for all diatomic molecules and even at very low temperatures for those not containing hydrogen, we may use the approximate forms for $\Theta_r \ll T$.

Now it can be shown that when $\Theta_r \ll T$ we have with a high degree of accuracy

$$\sum_{j=0,2,\ldots}^{\infty} (2j+1)\, e^{-j(j+1)\Theta_r/T} = \sum_{j=1,3,\ldots}^{\infty} (2j+1)\, e^{-j(j+1)\Theta_r/T}$$
$$= \frac{1}{2} \sum_{j=0,1,\ldots}^{\infty} (2j+1)\, e^{-j(j+1)\Theta_r/T}, \tag{315, 4}$$

and consequently the partition functions $r_n(T)$ for combined rotations and nuclear spins have the form

*Heteronuclear* $\qquad r_n(T) = r(T)\,\rho_a\rho_b;$ $\qquad$ (315, 5)

*Homonuclear* $\qquad r_n(T) = \frac{1}{2}r(T)\,\rho^2;$ $\qquad$ (315, 6)

where $r(T)$ is defined by

$$r(T) = \sum_{j=0,1,\ldots}^{\infty} (2j+1)\, e^{-j(j+1)\Theta_r/T}. \tag{315, 7}$$

This analysis has required a broadening of the classification of the states of a rotating homonuclear molecule, with which we shall be further concerned in Chapter v. We have hitherto treated atomic nuclei as structureless points, a treatment which has proved inadequate. When a nucleus has $\rho$ possible orientations, it must be assigned a weight $\rho$ times as great as we have hitherto used for structureless points. The diatomic molecule therefore should have a weight $\rho_a \rho_b$ due to the orientations of the nuclei. The extra factor $\rho^2$ is in homonuclear molecules reduced alternately to $\frac{1}{2}\rho(\rho-1)$ and $\frac{1}{2}\rho(\rho+1)$ by the requirements of symmetry in the nuclei, and therefore effectively to $\frac{1}{2}\rho^2$, except at very low temperatures. This reduction from $\rho^2$ to $\frac{1}{2}\rho^2$ is the quantal analogue of the introduction of the symmetry number $\sigma$ of classical statistics.*

We accordingly define a symmetry number $\sigma$ equal to 2 if the two nuclei in the molecule are identical and equal to 1 otherwise. We can now combine (5) and (6) into the single formula

$$r_n(T) = r(T)\,\rho_a \rho_b/\sigma, \tag{315, 8}$$

where $r(T)$ is defined by (7). Using formula (313, 3) for $r(T)$ in (8) we have

$$r_n(T) = \frac{T}{\Theta_r}\left\{1 + \frac{1}{3}\frac{\Theta_r}{T} + \frac{1}{15}\frac{\Theta_r^2}{T^2} + O\left(\frac{\Theta_r}{T}\right)^3\right\}\frac{\rho_a \rho_b}{\sigma} \quad (\Theta_r \ll T). \tag{315, 9}$$

In most cases it will be sufficient to retain only the first term, so that

$$r_n(T) = \frac{T}{\Theta_r}\frac{\rho_a \rho_b}{\sigma} = \frac{8\pi^2 AkT}{h^2}\frac{\rho_a \rho_b}{\sigma}, \tag{315, 10}$$

and we shall usually assume this approximation.

It has been tacitly assumed that the electronic eigen function, which is necessarily antisymmetrical with respect to any pair of electrons, is symmetrical with respect to the two identical nuclei of the diatomic molecule. This is in fact the case for the ground electronic state of most symmetrical diatomic molecules.

**§ 316. Amended formulae for monatomic molecules.** If we wish to bring our formulae of § 310 for monatomic molecules into line with those

* Ehrenfest and Trkal, *Proc. Sec. Sci. Amsterdam*, **23**, 162 (1920).

for diatomic molecules, we have merely to introduce the extra factor $\rho$ for the number of possible nuclear eigen functions. We have then for the complete partition function of a monatomic molecule

$$f(T) = \frac{(2\pi m kT)^{\frac{3}{2}} V}{h^3} \varpi_0 \rho, \tag{316, 1}$$

and so for the free energy of a gas with monatomic molecules

$$F = NkT\left\{\log \frac{N}{V} - 1\right\} - \tfrac{3}{2}NkT\log T - NkT\log\left\{\frac{(2\pi mk)^{\frac{3}{2}}}{h^3}\varpi_0\rho\right\}. \tag{316, 2}$$

For its partial potential we have

$$\mu = kT\log\frac{N}{V} - \tfrac{3}{2}kT\log T - kT\log\left\{\frac{(2\pi mk)^{\frac{3}{2}}}{h^3}\varpi_0\rho\right\}$$

$$= kT\log p - \tfrac{5}{2}kT\log T - kT\log\left\{\frac{(2\pi m)^{\frac{3}{2}}k^{\frac{5}{2}}}{h^3}\varpi_0\rho\right\}, \tag{316, 3}$$

and for its absolute activity $\lambda$,

$$\lambda = pT^{-\frac{5}{2}}\frac{h^3}{(2\pi m)^{\frac{3}{2}}k^{\frac{5}{2}}\varpi_0\rho}. \tag{316, 4}$$

We shall return to these formulae in Chapter v.

**§ 317. Final formulae for diatomic molecules at moderate temperatures.** When we take account of nuclear spins and symmetry, the complete partition function for a diatomic molecule becomes

$$f(T) = \frac{(2\pi mkT)^{\frac{3}{2}} V}{h^3} r_n(T)\varpi_0, \tag{317, 1}$$

where $r_n(T)$ is given by one of the formulae (315, 1), (315, 2), or (315, 3). Except for the $H_2$, $D_2$ and HD molecules at low temperatures we may safely use formulae (315, 8) and (315, 9) for $r_n(T)$, so that we have

$$f(T) = \frac{(2\pi mkT)^{\frac{3}{2}} V}{h^3} r(T)\varpi_0\frac{\rho_a\rho_b}{\sigma}$$

$$= \frac{(2\pi mkT)^{\frac{3}{2}} V}{h^3}\frac{T}{\Theta_r}\left\{1 + \frac{1}{3}\frac{\Theta_r}{T} + \frac{1}{15}\frac{\Theta_r^2}{T^2} + O\left(\frac{\Theta_r}{T}\right)^3\right\}\varpi_0\frac{\rho_a\rho_b}{\sigma}. \tag{317, 2}$$

Furthermore, except for molecules with a small moment of inertia, we may use the simpler approximation (315, 10) so that

$$f(T) = \frac{(2\pi mkT)^{\frac{3}{2}} V}{h^3}\frac{8\pi^2 AkT}{h^2}\varpi_0\frac{\rho_a\rho_b}{\sigma}. \tag{317, 3}$$

For the free energy we have according to (225, 4)

$$F = NkT\left\{\log\frac{N}{V}-1\right\}-\tfrac{5}{2}NkT\log T - NkT\log\left\{\frac{(2\pi mk)^{\frac{3}{2}}}{h^3}\frac{8\pi^2 Ak}{h^2}v_0\frac{\rho_a\rho_b}{\sigma}\right\}, \tag{317, 4}$$

and for the energy

$$E = -T^2\frac{\partial(F/T)}{\partial T} = \tfrac{5}{2}NkT. \tag{317, 5}$$

For the partial potential we have

$$\mu = (\partial F/\partial N)_{T,V} = kT\log\frac{N}{V} - \tfrac{5}{2}kT\log T - kT\log\left\{\frac{(2\pi mk)^{\frac{3}{2}}}{h^3}\frac{8\pi^2 Ak}{h^2}v_0\frac{\rho_a\rho_b}{\sigma}\right\}$$

$$= kT\log p - \tfrac{7}{2}kT\log T - kT\log\left\{\frac{(2\pi m)^{\frac{3}{2}}k^{\frac{5}{2}}}{h^3}\frac{8\pi^2 Ak}{h^2}v_0\frac{\rho_a\rho_b}{\sigma}\right\}, \tag{317, 6}$$

and for the absolute activity

$$\lambda = pT^{-\frac{7}{2}}\frac{h^3}{(2\pi m)^{\frac{3}{2}}k^{\frac{5}{2}}}\frac{h^2}{8\pi^2 Ak}\frac{\sigma}{v_0\rho_a\rho_b}. \tag{317, 7}$$

We shall return to these formulae in Chapter v.

Finally for the molecular heat capacity at constant volume of a diatomic gas

$$C_V = \tfrac{5}{2}k, \tag{317, 8}$$

and so, by (309, 6), for the molecular heat capacity at constant pressure

$$C_P = \tfrac{7}{2}k. \tag{317, 9}$$

These classical formulae are accurate as long as $T \gg \Theta_r$. When $\Theta_r/T$ is not entirely negligible compared with unity, we have to use (2) instead of (3) for the partition function. This adds to the free energy given by (4) the extra term

$$kT\log\left\{1+\frac{1}{3}\frac{\Theta_r}{T}+\frac{1}{15}\frac{\Theta_r^2}{T^2}+O\left(\frac{\Theta_r}{T}\right)^3\right\}$$

$$= -k\Theta_r\left\{\frac{1}{3}+\frac{1}{90}\frac{\Theta_r}{T}+O\left(\frac{\Theta_r}{T}\right)^2\right\} \quad (\Theta_r \ll T). \tag{317, 10}$$

We then deduce for the energy and heat capacity

$$\frac{E}{N} = -\frac{T^2}{N}\frac{\partial(F/T)}{\partial T} = \tfrac{5}{2}kT - k\Theta_r\left\{\frac{1}{3}+\frac{1}{45}\frac{\Theta_r}{T}+O\left(\frac{\Theta_r}{T}\right)^2\right\} \quad (\Theta_r \ll T), \tag{317, 11}$$

$$C_V = \frac{1}{N}\frac{\partial E}{\partial T} = k\left\{\frac{5}{2}+\frac{1}{45}\frac{\Theta_r^2}{T^2}+O\left(\frac{\Theta_r}{T}\right)^3\right\} \quad (\Theta_r \ll T). \tag{317, 12}$$

It should be noticed that $C_V$ approaches its classical value $\frac{5}{2}k$ from above. We would emphasize that formulae (11) and (12) and similar formulae must not be used unless $\Theta_r \ll T$. As long as $\Theta_r \ll T$, formulae such as (315, 4) and (315, 9) are accurate, but it would be wrong to argue that when $\Theta_r = \frac{1}{2}T$,

because the second term in (12) is only 0·005, therefore the deviation of $C_V$ from its classical value $\frac{5}{2}k$ is negligible.*

At much lower temperatures such that $T \ll \Theta_r$ the rotational partition function reduces to its lowest term. The rotational contribution $C^{\text{rot}}$ to the molecular heat capacity falls to zero, and $C_V$ falls to $\frac{3}{2}k$.

At intermediate temperatures there is no compact formula for $C^{\text{rot}}$.

**§ 318. Heat capacities of typical diatomic molecules.** At temperatures such that the two rotational degrees of freedom are classical and the vibrational degree of freedom is unexcited, we have formulae (317, 8) and (317, 9) for $C_V$ and $C_P$, with the consequent value for their ratio

$$\gamma = C_P/C_V = \tfrac{7}{5}. \tag{318, 1}$$

The data in Table 2 show that these values agree with experiment for many diatomic molecules over a wide range of temperatures. The third column will be required for the discussion in § 323.

TABLE 2

*Values of $C_P$ and of $\gamma$ for diatomic gases*

Theoretical values: $C_P/k$ = 3·50 and $\gamma = C_P/C_V$ = 1·40

| Substance | $\Theta_r$ deg. | $\Theta_v/10^3$ deg. | Temp. °K. | $C_P/k$ obs. | $\gamma$ obs. | Observer |
|---|---|---|---|---|---|---|
| $H_2$ | 85·4 | 6·10 | 289 | 3·45 | - | S.H. |
| $N_2$ | 2·86 | 3·34 | 293 | 3·51 | - | S.H. |
| | | | 92 | 3·38 | | S.H. |
| $O_2$ | 2·07 | 2·23 | 293 | 3·51 | | S.H. |
| | | | 197 | 3·43 | – | S.H. |
| | | | 92 | 3·47 | — | S.H. |
| CO | 2·77 | 3·07 | 291 | 3·52 | | S.H. |
| | | | 93 | 3·40 | | S.H. |
| NO | 2·42 | 2·69 | 288 | 3·64 | | H. |
| HCl | 15·2 | 4·14 | 290–373 | — | 1·39 | S. |
| HBr | 12·1 | 3·7 | 284–373 | — | 1·43 | S. |
| HI | 9·0 | 3·2 | 293–373 | — | 1·40 | S. |

*References to Table 2*

S.H. Scheel and Heuse, *Ann. d Phys.* **40**, 473 (1913).
H. Heuse, *Ann. d. Phys.* **59**, 86 (1919).
S. Strecker, *Ann. d. Phys.* **17**, 85 (1882).

* The difference between the sums $\sum_{j=0,2,\dots}$ and $\sum_{j=1,3,\dots}$ in (315, 4) is a $\Theta$ function and so vanishes exponentially when $\Theta_r/T \to 0$. It is however necessary for $\Theta_r$ to be less than about $\frac{1}{4}T$ before it is a reasonable approximation to assume that $\sum_{j=0,2,\dots} = \sum_{j=1,3,\dots}$, and this approximation is involved in the application of formulae such as (11) and (12) to symmetrical molecules.

**§ 319. Heat capacity of hydrogen and deuterium at low temperatures. Para and ortho forms of $H_2$ and $D_2$.** The predicted drop in the molecular heat capacity $C_V$ from $\frac{5}{2}k$ at ordinary temperatures to $\frac{3}{2}k$ at low temperatures has been observed for $H_2$, $D_2$ and HD alone among diatomic gases. The molecular heat capacity $C_V$ has approximately the normal value for $H_2$ at ordinary temperatures of 300° K. and above, but falls steadily to $\frac{3}{2}k$ as $T$ diminishes. For temperatures below 40° K. $C_V$ and $\frac{3}{2}k$ are indistinguishable. The general behaviour is accounted for if we may identify the variable part of $C_V$ with $C^{\mathrm{rot}}$ and apply the foregoing theory. The successful detailed theory is, however, more subtle and is due to Dennison.* From the study of the rotational bands of $H_2$ we know that $\rho = 2$ for the proton. This requires for the rotational-nuclear partition function of $H_2$, according to (315, 2),

$$r_n(T) = 1 \sum_{j=0,2,\ldots}^{\infty} (2j+1)\, e^{-j(j+1)\Theta_r/T} + 3 \sum_{j=1,3,\ldots}^{\infty} (2j+1)\, e^{-j(j+1)\Theta_r/T}, \quad (319, 1)$$

$\Theta_r$ being defined by (313, 2). Partition functions of this form were examined by Hund,† but were found to give curves bearing no resemblance whatever to the observations. To apply the theory properly one further point must be made. While there is no doubt that the possible states are correctly enumerated in (1), it is also assumed in (1) that interchanges between all the states of (1) take place freely, so that the distribution laws of the observed state are correctly given by (1) at all temperatures. But it is necessary to ask whether these interchanges can occur freely at ordinary and low temperatures; actually even at high temperatures interchanges between the symmetrical and antisymmetrical rotational states are rare, except in the presence of a catalyst, because the fastest mechanism for interchange involves free H atoms. Collisions between two molecules without dissociation result in interchanges with a frequency proportional to the perturbation of the energy values of the molecules by the magnetic moments associated with the nuclear spins —that is much less frequently than interchanges between the states of para- and ortho-helium. Thus in ordinary hydrogen gas, interchanges between the symmetrical and antisymmetrical states occur to an appreciable extent only in times long compared with the time of an experiment The heat capacity measurements are therefore made on a gas, which is not in the true equilibrium state governed by (1), but is in a metastable equilibrium behaving as a mixture of two substances. The one with antisymmetrical spin eigen functions (nuclear singlets) is called para-hydrogen, the one with symmetrical spin eigen functions (nuclear triplets) is called ortho-hydrogen. Para-hydrogen has only

* Dennison, *Proc. Roy. Soc.* A, **115**, 483 (1927)
† Hund, *Zeit. f. Physik.* **42**, 93 (1927)

symmetrical (even numbered) rotational states, and ortho-hydrogen only antisymmetrical (odd numbered) rotational states. For para-hydrogen we have the nuclear weight $\frac{1}{2}\rho(\rho-1) = 1$ and the rotational-nuclear partition function

$$r_p(T) = 1 \cdot \sum_{j=0,2,\ldots}^{\infty} (2j+1)\, e^{-j(j+1)\Theta_r/T}, \tag{319, 2}$$

whereas for ortho-hydrogen we have the nuclear weight $\frac{1}{2}\rho(\rho+1) = 3$ and the rotational-nuclear partition function

$$3r_o(T) = 3 \cdot \sum_{j=1,3,\ldots}^{\infty} (2j+1)\, e^{-j(j+1)\Theta_r/T}. \tag{319, 3}$$

The rotational energy of pure para-hydrogen would be

$$E_p^{\text{rot}} = NkT^2 \frac{\partial \log r_p(T)}{\partial T}, \tag{319, 4}$$

and that of pure ortho-hydrogen would be

$$E_o^{\text{rot}} = NkT^2 \frac{\partial \log 3r_o(T)}{\partial T}. \tag{319, 5}$$

The corresponding rotational molecular heat capacities would be, for pure para-hydrogen,

$$C_p^{\text{rot}} = k \frac{\partial}{\partial T}\left\{T^2 \frac{\partial \log r_p(T)}{\partial T}\right\}, \tag{319, 6}$$

and, for pure ortho-hydrogen,

$$C_o^{\text{rot}} = k \frac{\partial}{\partial T}\left\{T^2 \frac{\partial \log 3r_o(T)}{\partial T}\right\}. \tag{319, 7}$$

Consequently that of the actual mixture of para- and ortho-hydrogen in the ratio 1 : 3 will be

$$C^{\text{rot}} = \tfrac{1}{4}C_p^{\text{rot}} + \tfrac{3}{4}C_o^{\text{rot}}. \tag{319, 8}$$

The result of using (8) with $A = 0{\cdot}463 \times 10^{-40}$ g.cm.$^2$ is the set of points shown by crosses in Fig. 1. The agreement with experiment is all that can be desired.

The two modifications of $H_2$, first postulated to explain the heat capacity curve, are nowadays familiar chemical substances.* The metastable equilibrium of $H_2$ has further important consequences to which we must return in Chapter v in discussing Nernst's Heat Theorem.

Thanks to the discovery of deuterium, two other diatomic molecules, HD and $D_2$, are now known, whose rotational heat capacities fall below the classical value at low temperatures. For HD the simple partition function (315, 1) should yield the correct heat capacity, since this heteronuclear molecule has no rotational symmetry requirements. Fig. 2 shows this

* For a recent account of the many interesting properties of para and ortho hydrogen see Farkas. *Orthohydrogen, Parahydrogen and Heavy Hydrogen* (Cambridge, 1935).

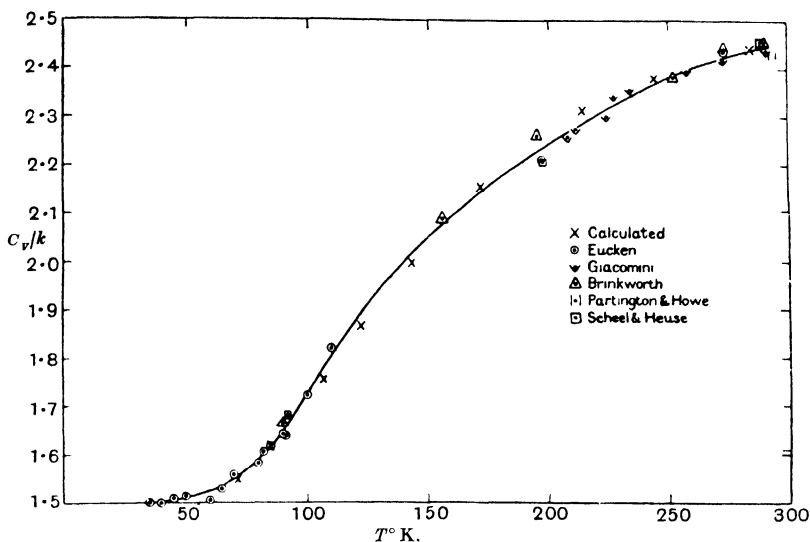



Fig. 1. The molecular heat capacity of hydrogen.

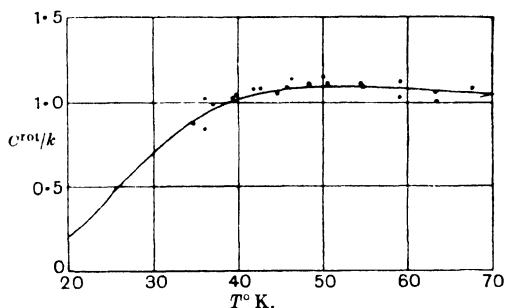



Fig. 2. The rotational molecular heat capacity of HD.

curve and the observations of Clusius and Bartholomé.* The agreement is excellent; in particular the existence of the maximum is clearly shown. For $D_2$ symmetry requirements return. It is found that for the D nuclei $\rho = 3$, so the nuclear spin weights in the molecule are

$$\tfrac{1}{2}\rho(\rho-1) = 3 \quad \text{(para-deuterium)}, \qquad (319, 9)$$

$$\tfrac{1}{2}\rho(\rho+1) = 6 \quad \text{(ortho-deuterium)}. \qquad (319, 10)$$

Since the mass number of deuterium is even, the complete eigen functions

* Clusius and Bartholomé, *Zeit. Elektrochem.* **40**, 524 (1934).

must be symmetrical in the nuclei. The rotational-nuclear partition functions are therefore

$$3r_p(T) = 3 \cdot \sum_{j=1,3,\dots}^{\infty} (2j+1)\, e^{-j(j+1)\Theta_r/T}, \tag{319, 11}$$

$$6r_o(T) = 6 \cdot \sum_{j=0,2,\dots}^{\infty} (2j+1)\, e^{-j(j+1)\Theta_r/T}, \tag{319, 12}$$

the odd rotational states occurring in para-deuterium and the even in ortho-deuterium. At high temperatures the ratio of ortho to para molecules is 6 : 3 or 2 : 1. For the rotational molecular heat capacities of the pure para and ortho forms we have therefore

$$C_p^{\text{rot}} = k \frac{\partial}{\partial T}\left(T^2 \frac{\partial \log 3r_p(T)}{\partial T}\right), \tag{319, 13}$$

$$C_o^{\text{rot}} = k \frac{\partial}{\partial T}\left(T^2 \frac{\partial \log 6r_o(T)}{\partial T}\right). \tag{319, 14}$$

The rotational molecular heat capacity of the ordinary metastable mixture is then given by

$$C^{\text{rot}} = \tfrac{1}{3}C_p^{\text{rot}} + \tfrac{2}{3}C_o^{\text{rot}}. \tag{319, 15}$$

The theoretical values and the observations of Clusius and Bartholomé* are shown in Fig. 3. The agreement is again excellent. The broken curves correspond to alternative assumed values of $\rho$.

As a final illustration we show in Fig. 4 the rotational heat capacities of pure ortho- and para-$H_2$, ortho- and para-$D_2$, HD, and the metastable mixtures of ortho- and para-$H_2$ and $D_2$ drawn to the same temperature scale.

The temperature at which $C^{\text{rot}}$ begins to deviate appreciably from its classical value $k$ is roughly proportional to $\Theta_r$, and may be taken as not more than 3 to 4 times $\Theta_r$. The moment of inertia of $H_2$ is smaller than that of any other diatomic molecule and $C^{\text{rot}}/k$ is effectively unity for $H_2$ above 300° K. From the values of $\Theta_r$ given in Table 2 we can therefore see that, even for such a molecule as HCl, $C^{\text{rot}}/k$ will be effectively classical above 50° K. Observations of non-classical values of $C^{\text{rot}}$ are therefore evidently difficult for all diatomic molecules other than $H_2$, $D_2$ and HD. The absence of other examples of a non-classical value of $C^{\text{rot}}/k$ in gases is therefore in accordance with the theory.

**§ 320. Vibrational degree of freedom.** It may happen at high temperatures that the vibrational degree of freedom of a diatomic molecule is not entirely unexcited. As a rough approximation we suppose the vibrational and rotational motions to be independent of each other. The more

* Clusius and Bartholomé, *Zeit. Elektrochem.* **40**, 524 (1934).

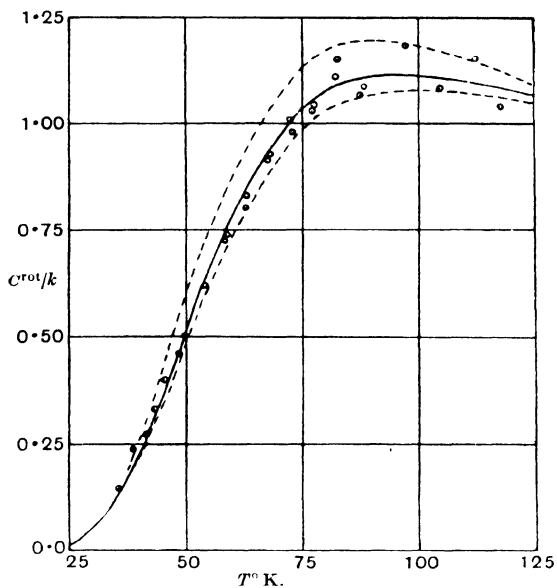



Fig. 3. The rotational molecular heat capacity of $D_2$.

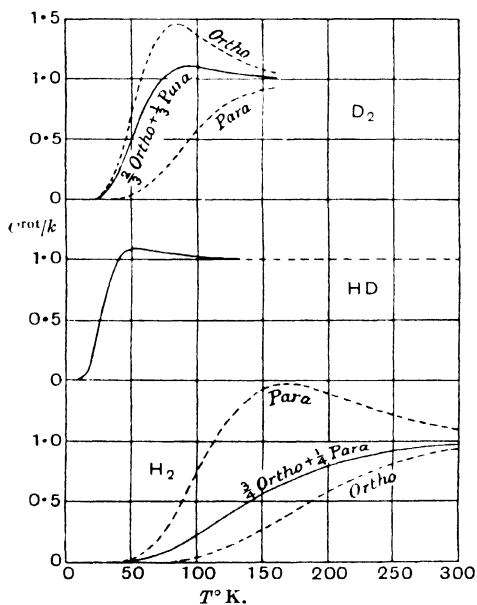



Fig. 4. Theoretical rotational molecular heat capacities of $H_2$, HD and $D_2$.

rigid the molecule and the higher the vibrational frequency, the better is this approximation. We also suppose that the vibrations are those of a simple harmonic oscillator of frequency $\nu$, but that, as an energy $\chi$ will dissociate the molecule, not more than $p$ states are possible in which the molecule remains a molecule. Actually the energy levels converge to the limit $\chi$, but this approximation will suffice. If then we take our energy zero as that of the lowest vibrational state (not a state of no vibration), the vibrational partition function will be

$$q(T) = \sum_{v=0}^{p-1} e^{-vh\nu/kT} = \frac{1-e^{-ph\nu/kT}}{1-e^{-h\nu/kT}}. \qquad (320, 1)$$

If $\chi$ or $ph\nu$ is fairly large compared with $h\nu$, there will be a considerable range of values of $T$ where $e^{-ph\nu/kT}$ is negligible compared with 1, while $e^{-h\nu/kT}$ is not. For such temperatures $q(T)$ reduces to the complete partition function for a simple harmonic oscillator

$$q(T) = (1-e^{-h\nu/kT})^{-1}, \qquad (320, 2)$$

and over this temperature region this form will be a good approximation to more exact forms of the vibrational partition function. When we use this form for the vibrational partition function, we find for the equilibrium contribution, $E^{\text{vib}}$, of the vibrations to the energy of $N$ molecules

$$E^{\text{vib}} = NkT^2 \frac{\partial \log q(T)}{\partial T} = N\frac{h\nu}{e^{h\nu/kT}-1}, \qquad (320, 3)$$

with the limiting forms

$$E^{\text{vib}} = 0 \quad (kT \ll h\nu), \qquad (320, 4)$$

$$E^{\text{vib}} = NkT - N\tfrac{1}{2}h\nu + O(1/T) \quad (kT \gg h\nu). \qquad (320, 5)$$

If we take as the zero of energy, not the lowest quantum state, but the state of rest at the position of minimum potential energy, the vibrational partition function becomes

$$q(T) = e^{-\frac{1}{2}h\nu/kT}(1-e^{-h\nu/kT})^{-1} = 1/2\sinh(\tfrac{1}{2}h\nu/kT). \qquad (320, 6)$$

We now obtain for the vibrational contribution to the energy

$$E^{\text{vib}} = NkT^2 \frac{\partial \log q(T)}{\partial T} = NkT\frac{(\frac{1}{2}h\nu/kT)\cosh(\frac{1}{2}h\nu/kT)}{\sinh(\frac{1}{2}h\nu/kT)}, \qquad (320, 7)$$

with the limiting forms

$$E^{\text{vib}} = N\tfrac{1}{2}h\nu \quad (kT \ll h\nu), \qquad (320, 8)$$

$$E^{\text{vib}} = NkT + O(1/T) \quad (kT \gg h\nu). \qquad (320, 9)$$

Formula (8) merely states that the vibrational energy at the absolute zero (*Nullpunktsenergie*) is equal to the vibrational energy of the lowest energy level; this we shall call the *residual energy* of the vibrators. By

comparison of formulae (5) and (9) we observe that the classical value $NkT$ for the vibrational energy is more accurate when the state of rest at the equilibrium position is taken as energy zero, than when the lowest vibrational state is taken as energy zero.

**§ 321. Diatomic gases at high temperatures.** At high temperatures we can improve on our previous formulae for diatomic molecules by including the vibrational partition function. Besides the translations, rotations and vibrations, no other degree of freedom* can contribute to the partition function at temperatures below 10,000° K. Using (320, 2) for the vibrational partition function we obtain for the resultant partition function

$$f(T) = \frac{(2\pi m kT)^{\frac{3}{2}} V}{h^3} \frac{8\pi^2 A kT}{h^2} (1 - e^{-h\nu/kT})^{-1} \varpi_0 \frac{\rho_a \rho_b}{\sigma}. \qquad (321, 1)$$

It should be emphasized that the energy zero is here taken to be that of a molecule in its lowest quantum state.

For the free energy we have

$$F = NkT\left(\log \frac{N}{V} - 1\right) - \tfrac{5}{2}NkT \log T + NkT \log(1 - e^{-h\nu/kT})$$
$$- NkT \log\left\{\frac{(2\pi mk)^{\frac{3}{2}}}{h^3} \frac{8\pi^2 Ak}{h^2} \varpi_0 \frac{\rho_a\rho_b}{\sigma}\right\}. \qquad (321, 2)$$

The corresponding formula for the partial potential is

$$\mu = \left(\frac{\partial F}{\partial N}\right)_{T,V} = kT \log \frac{N}{V} - \tfrac{5}{2}kT \log T + kT \log(1 - e^{-h\nu/kT})$$
$$- kT \log\left\{\frac{(2\pi mk)^{\frac{3}{2}}}{h^3} \frac{8\pi^2 Ak}{h^2} \varpi_0 \frac{\rho_a\rho_b}{\sigma}\right\}$$
$$= kT \log p - \tfrac{7}{2}kT \log T + kT \log(1 - e^{-h\nu/kT})$$
$$- kT \log\left\{\frac{(2\pi m)^{\frac{3}{2}} k^{\frac{5}{2}}}{h^3} \frac{8\pi^2 Ak}{h^2} \varpi_0 \frac{\rho_a\rho_b}{\sigma}\right\}. \qquad (321, 3)$$

For the total energy, referred to the lowest vibrational state as energy zero, we have

$$E = -T^2 \frac{\partial(F/T)}{\partial T} = N\left\{\tfrac{5}{2}kT + \frac{h\nu}{e^{h\nu/kT} - 1}\right\}, \qquad (321, 4)$$

and so for the molecular heat capacity

$$C_V = \frac{1}{N}\left(\frac{\partial E}{\partial T}\right)_V = k\left\{\frac{5}{2} + \left(\frac{1}{2}\frac{h\nu}{kT}\right)^2 \Big/ \sinh^2\left(\frac{1}{2}\frac{h\nu}{kT}\right)\right\}. \qquad (321, 5)$$

* $O_2$ and NO are exceptions. The electronic contributions of these molecules are discussed in § 325

We shall often find it convenient to define a temperature $\Theta$ related to a molecular energy $\epsilon$ by $\Theta = \epsilon/k$. We have in fact already used such a temperature $\Theta_r$ in our discussion of rotational motion. We now define a temperature $\Theta_v$ by

$$k\Theta_v = h\nu. \tag{321, 6}$$

We can call $\Theta_v$ the frequency measured in degrees. Values of $\Theta_v$ obtained from spectral data are given in Table 2 for the molecules there listed. In terms of $\Theta_v$ (5) can be written

$$C_P/k - \tfrac{7}{2} = C_V/k - \tfrac{5}{2} = \{(\tfrac{1}{2}\Theta_v/T)/\sinh(\tfrac{1}{2}\Theta_v/T)\}^2. \tag{321, 7}$$

We shall denote the contribution of the vibrational degree of freedom to the molecular heat capacity by $C^{\text{vib}}$. According to (7) we have the two limiting forms

$$C^{\text{vib}}/k = 0 \quad (T \ll \Theta_v), \tag{321, 8}$$

$$C^{\text{vib}}/k = 1 \quad (T \gg \Theta_v). \tag{321, 9}$$

At intermediate temperatures $C^{\text{vib}}/k$ is readily calculated* by means of formula (7). Its behaviour is shown by the values given in Table 3.

TABLE 3

*Vibrational contribution $C^{\text{vib}}$ to the heat capacity of a diatomic molecule as a function of the temperature*

| $T/\Theta_v$ | $\frac{1}{8}$ | $\frac{1}{4}$ | $\frac{1}{2}$ | 1 | 2 | 4 |
|---|---|---|---|---|---|---|
| $C^{\text{vib}}/k$ | 0·022 | 0·303 | 0·724 | 0·928 | 0·979 | 0·9995 |

**§ 322. Heat capacity of $H_2$ at high temperatures.** To obtain a satisfactory theoretical account of the heat capacity of $H_2$ at high temperatures it is not sufficient to treat the rotations and vibrations of the molecule as independent degrees of freedom. The quantitative a priori calculation of the energy levels by quantum theory is therefore not simple. From the point of view of *statistical* theory it is not necessary to go back to a mechanical model. It is sufficient to take the states of vibration and rotation of the normal $H_2$-molecule as enumerated directly from the band spectrum, to construct a semi-empirical partition function with their help, and to use this function to evaluate $C^{\text{rot}} + C^{\text{vib}}$. At these higher temperatures the differences between symmetrical and antisymmetrical rotational states are unimportant, and we may use without serious loss of accuracy the one partition function

$$\sum_{v=0}^{\infty} \sum_{j=0}^{\infty} (2j+1)\, e^{-\epsilon(v,j)/kT}, \tag{322, 1}$$

* The table given by Landolt-Bornstein is inaccurate in places.

where $v$ is the vibrational and $j$ the rotational quantum number, and $\epsilon(v, j)$, which represents the energies derived from the band spectrum, can be put in a simple polynomial form with sufficient accuracy. From this partition function the heat capacity has been computed by McCrea.* The results are compared with the experimental values in Table 4. The agreement is satisfactory especially at the higher temperatures where it would fail but for these theoretical refinements.

If it is desired to refer the energy values back to a model, it is necessary to assume a definite law of force between the nuclei. Such calculations have been made, for example, by Fues.†

TABLE 4

*Heat capacity of* $H_2$ *at high temperatures*

| Temp. °K. | $C_V/k$ calculated | $C_V/k$ observed‡ |
|---|---|---|
| 600 | 2·51 | 2·56 |
| 800 | 2·54 | 2·63 |
| 1000 | 2·60 | 2·70 |
| 1200 | 2·69 | 2·77 |
| 1600 | 2·88 | 2·91 |
| 1800 | 2·96 | 2·98 |
| 2000 | 3·05 | 3·05 |
| 2500 | 3·21 | 3·23 |

‡ According to an interpolation formula given by Partington and Shilling, *The Specific Heat of Gases* (Benn, 1924).

**§ 323. Heat capacities of other diatomic molecules at moderately high temperatures.** The same considerations can be applied to explain the heat capacities of other diatomic molecules at moderately high temperatures. At these temperatures rotations are completely classical and it is then unnecessary, as we have seen, to take account of any requirements of nuclear symmetry. A sufficiently accurate formula for $C_V$, at least for a first survey, is provided by (321, 7) with $\Theta_v$ defined by (321, 6). More accurate comparisons can be made if desired by the method described in § 322 for $H_2$. Such a laborious procedure is, however, usually unnecessary. Even when the simple formula (321, 7) is retained, one can usually make adequate allowance for anharmonicity as follows. The energy levels of an anharmonic oscillator can be expressed with sufficient accuracy in the form

$$\epsilon_v = (v+\tfrac{1}{2})\,h\nu_e\{1-(v+\tfrac{1}{2})\,x_e\}, \qquad (323, 1)$$

where $v$ is the vibrational quantum number, $\nu_e$ is a characteristic frequency,

* McCrea, *Proc. Camb. Phil. Soc.* **24**, 80 (1928), and since then by numerous other investigators in this field.

† Fues, *Ann. d. Phys.* **80**, 367 (1926).

and $x_e$ is an anharmonicity constant. In particular we have for the ground state

$$\epsilon_0 = \tfrac{1}{2}h\nu_e\{1 - \tfrac{1}{2}x_e\}, \qquad (323, 2)$$

and for the first excited state

$$\epsilon_1 = \tfrac{3}{2}h\nu_e\{1 - \tfrac{3}{2}x_e\}. \qquad (323, 3)$$

Even at temperatures as high as 2000° K. the main contribution to the vibrational partition function comes from the first two terms. Hence the most important energy separation is

$$\epsilon_1 - \epsilon_0 = h\nu_e\{1 - 2x_e\}. \qquad (323, 4)$$

We can therefore obtain accurate values for the heat capacity if we insert into formula (321, 7) a value of $\Theta_v$ given by

$$k\Theta_v = h\nu_e\{1 - 2x_e\}. \qquad (323, 5)$$

On the other hand the residual energy is given by (2). The values of $\Theta_v$ recorded in Table 2 are defined according to (5). Thus $k\Theta_v$ is the energy separation between the normal state and the first excited vibrational state.

It is only recently that satisfactory agreement has been reached between theory and experiment for heat capacities at high temperatures. One of the commonest methods used in the past for determining the heat capacity of a gas is by measuring the velocity of sound. The experimental values so obtained at high temperatures are in all cases considerably lower than the theoretical values. The reason for this is now understood. Except in hydrogen the rate of conversion of translational or rotational energy into vibrational energy by molecular collisions is unexpectedly slow.* Therefore, unless the time scale of the experiment is long compared with the time of adjustment of translational and vibrational energy, the true heat capacity will not be measured, but rather a heat capacity of a quasi-metastable state of the gas, in which the gas behaves as if it had no vibrational degrees of freedom. In the velocity of sound method the time scale is of the order $10^{-3}$ sec., equal to the period of the sound wave. This is too short a period for the internal vibrations to be maintained in thermal equilibrium with the translations and rotations. Measurements of the velocity of sound therefore lead to values of the heat capacities lower than the true equilibrium values.

We observe that we have here our second example of the care that is necessary in defining accessible states of an assembly. We have already observed that for hydrogen at ordinary pressures and low temperatures, in the absence of any catalyst, we can specify the effectively accessible states of the assembly correctly, only by regarding the hydrogen as a mixture of

* This has been established theoretically by the work of Herzfeld and Rice, Zener and others; e.g. Herzfeld and Rice, *Phys. Rev.* **31**, 691 (1928); Zener, *Phys. Rev.* **37**, 556; **38**, 277 (1931).

two distinct gases para-hydrogen and ortho-hydrogen. This specification is correct unless we experiment on a time scale of the order of days or weeks. We now find that for ordinary diatomic gases, analysed by sound waves of periods about $10^{-3}$ sec. or less, at temperatures of the order of 300–500° K., there is effectively no interconnection between the different vibrational states; the accessible states of the assembly are those of a mixture of distinct gases, each of given vibrational energy, and the molecular heat capacity $C_V$ is given by $C_V/k = \frac{5}{2}$. If, however, we increase the experimental time to 1 sec., the accessible states are effectively those of a single gas. If the accessible states are correctly specified, we can correctly treat either extreme case —the true equilibrium states or the perfect metastable equilibrium state— by the methods of statistical mechanics, and the calculations so made may be compared with the results of experiments made on a suitable time scale. But the intermediate cases, where there is a partial adjustment between different types of states, can never be so treated. Their treatment requires always a knowledge of rates of interaction, foreign to pure equilibrium theory, which from this point of view deals always with assemblies whose rates of interaction between states may all be classified as either infinitely fast or infinitely slow.

We pass on now to compare theory with experiment. If we plot $C_P/k$ against $T/\Theta_v$, we should according to theory obtain the same curve, given by formula (321, 7), for all diatomic gases. The experimental data suitable for comparison with theory have been so plotted in Fig. 5. The values of $\Theta_v$ determined spectroscopically for the several molecules are given in Table 2. Chlorine was not included in this table because, owing to its low value 798 of $\Theta_v$, the vibrational contribution $C^{\text{vib}}$ to the heat capacity is not negligible even at the lowest temperatures at which measurements have been made. We see from Fig. 5 that the agreement with the theoretical curve is good, especially when one remembers that a discrepancy of 0·05 in $C^{\text{vib}}/k$ corresponds to one of only about $1\frac{1}{2}$ % in the measured $C_P$. The data of Henry* were obtained by a flow method, and are therefore particularly suitable for comparison with the theory. Those of Eucken† and his collaborators were obtained by an adiabatic expansion method, and their values, extrapolated to zero pressure, are in excellent agreement with the theoretical values. The data of Sherratt and Griffiths‡ for CO are also suitable for comparison with theory. It is true that these are measurements of the velocity of sound and are therefore not of a sufficiently slow time scale to give directly the

* Henry, *Proc. Roy. Soc.* A, **133**, 492 (1931). Also private communication of later results

† Eucken and von Lüde, *Zeit. Physikal. Chem.* B, **5**, 413 (1929); Eucken and Hoffmann, *Zeit. Physikal. Chem.* B, **5**, 442 (1929).

‡ Sherratt and Griffiths, *Proc. Roy. Soc.* A, **147**, 292 (1934).

true equilibrium heat capacity. But as the velocity was measured for two frequencies of the sound waves, it was possible to apply a theoretical formula to extrapolate to zero frequency. It is these extrapolated values which can correctly be compared with the theoretical values, and are included in Fig. 5.

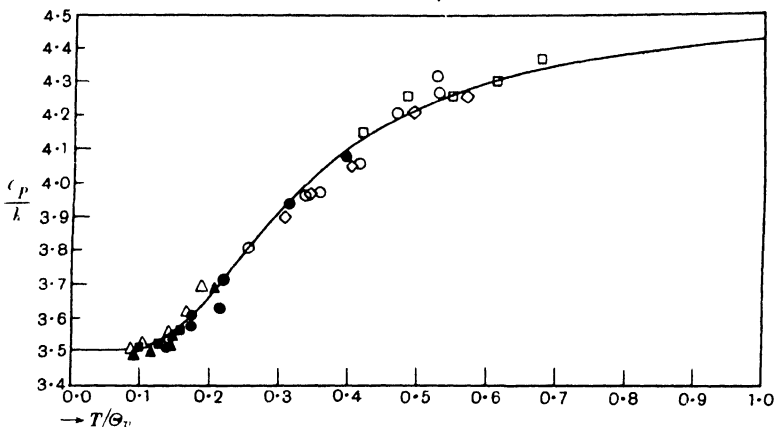



Fig. 5. Molecular heat capacities of diatomic gases.
Henry: ○ $O_2$; △ $N_2$. Eucken and others: ● $O_2$; ▲ $N_2$; ■ CO; ◇ $Cl_2$.
Sherratt and Griffiths: □ CO.

**§ 324. Electronic contributions.** As already mentioned in § 308, it may happen that other electron levels besides the lowest contribute appreciably to the partition function. This may be the case when the normal state forms part of a multiplet. We shall consider the particular case where it forms part of a doublet. The extension to triplets or higher multiplets will be obvious. For convenience we take our zero of energy as that of the normal state, that is the lower state of the doublet. Let the energy of the higher state of the doublet be $\epsilon_1$. Then the electronic partition function will be

$$e(T) = \varpi_0 + \varpi_1 e^{-\epsilon_1/kT}, \tag{324, 1}$$

where $\varpi_0$ and $\varpi_1$ are the weights of the two component states of the electronic doublet. Consequently the free energy will contain instead of $-NkT\log\varpi_0$ the term

$$F^{\text{el}} = -NkT\log(\varpi_0 + \varpi_1 e^{-\epsilon_1/kT}), \tag{324, 2}$$

and the energy will contain the extra term

$$E^{\text{el}} = -\frac{T^2\,\partial(F^{\text{el}}/T)}{\partial T} = \frac{N\epsilon_1}{1+(\varpi_0/\varpi_1)\,e^{\epsilon_1/kT}}. \tag{324, 3}$$

The molecular heat capacity will contain the term

$$C^{\text{el}} = \frac{1}{N}\frac{\partial E^{\text{el}}}{\partial T} = k\frac{(\epsilon_1/kT)^2}{\{1+(\varpi_0/\varpi_1)\,e^{\epsilon_1/kT}\}\{1+(\varpi_1/\varpi_0)\,e^{-\epsilon_1/kT}\}}. \tag{324, 4}$$

Examples of this are shown in Fig. 6. It is clear from (4) that $C^{el}$ vanishes both for large and small values of $kT/\epsilon_1$, and is only sensible when $kT$ is of the same order as $\epsilon_1$. When $kT \ll \epsilon_1$ the upper state of the doublet may be ignored; when $kT \gg \epsilon_1$ the distinction between the two states may be ignored, and the combined multiplet regarded as a single state of weight $\varpi_0 + \varpi_1$.

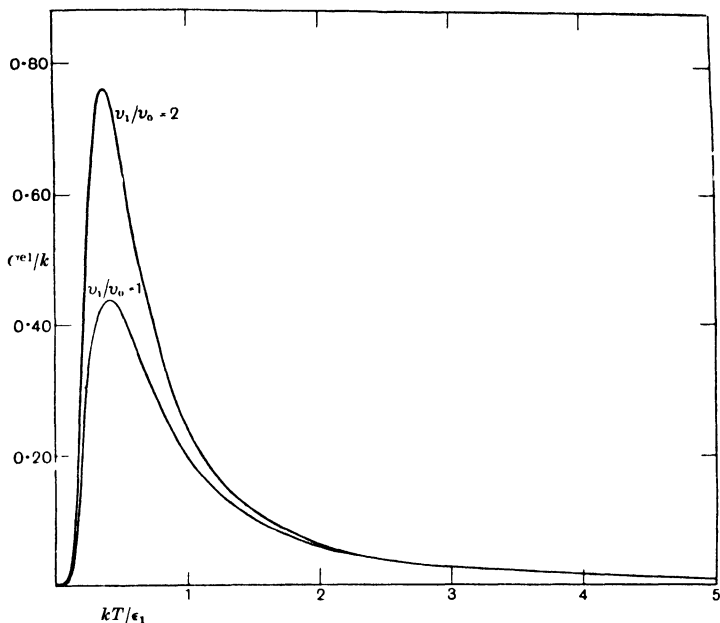



Fig. 6. The value of $C^{el}/k$ as a function of $kT/\epsilon_1$, calculated according to equation (324,4).

**§ 325. Application to molecules in multiplet states.** Thallium is an example of a monatomic molecule in a state forming part of a doublet. The normal electronic state is $^2P_{\frac{1}{2}}$, but the $^2P_{\frac{3}{2}}$ state, the upper state of the doublet, lies not far above. The weights of these two states are 2 and 4 respectively. The electronic partition function is therefore

$$2 + 4e^{-\epsilon_1/kT}. \qquad (325,1)$$

There are no experimental data for either thallium or any other monatomic molecule to compare with a formula such as (1). We may, however, apply these formulae to NO whose normal state $^2\Pi_{\frac{1}{2}}$ belongs to the doublet $^2\Pi_{\frac{1}{2},\frac{3}{2}}$, each component having an electronic weight 2. Actually the electronic angular momentum (of orbit and of spin) combines vectorially with the angular momentum of the rotating nuclei, and since the two are at right angles to each other, the resultant total angular momentum cannot be less

than the electronic contribution. The minimum values of the rotational quantum number $j$ are consequently $\frac{1}{2}$ for the $^2\Pi_{\frac{1}{2}}$ component of the electronic doublet and $\frac{3}{2}$ for the $^2\Pi_{\frac{3}{2}}$ component. If we take the lowest state as energy zero, and denote by $\epsilon_1$ the energy separation of the electronic doublet, we have for the combined electronic and rotational partition function

$$2\sum_{j=\frac{1}{2},\frac{3}{2},\dots}(2j+1)\,e^{-j(j+1)\Theta_r/T}+2e^{-\epsilon_1/kT}\sum_{j=\frac{3}{2},\frac{5}{2},\dots}(2j+1)\,e^{-j(j+1)\Theta_r/T} \qquad (325,2)$$

At ordinary temperatures, when $T \gg \Theta_r$, we can replace the sums by integrals, and each integral becomes approximately $T/\Theta_r$. Formula (2) thus reduces to

$$r(T)\,e(T) = \frac{T}{\Theta_r}e(T), \qquad (325,3)$$

where the electronic partition function $e(T)$ is defined by

$$e(T) = 2+2e^{-\epsilon_1/kT}. \qquad (325,4)$$

We therefore have the complete partition function

$$f(T) = \frac{(2\pi mkT)^{\frac{3}{2}}\,V}{h^3}\frac{8\pi^2 A\,kT}{h^2}(2+2e^{-\epsilon_1/kT})\,\rho_N\rho_O, \qquad (325,5)$$

where $\rho_N$, $\rho_O$ are the nuclear spin weights of $N$, $O$ respectively. We shall return to the use of (5) in Chapter V. At this stage we shall consider only the heat capacities. We derive from (5)

$$C_v/k = \frac{5}{2}+\frac{(\epsilon_1/kT)^2}{(1+e^{\epsilon_1/kT})(1+e^{-\epsilon_1/kT})}$$

$$= \frac{5}{2}+\frac{(\epsilon_1/2kT)^2}{\cosh^2(\epsilon_1/2kT)}. \qquad (325,6)$$

The second term $C^{\mathrm{el}}/k$ has its maximum value 0·44 when $\epsilon_1/kT = 2{\cdot}4$. For NO we have $\epsilon_1/k = 178^\circ$ K. Consequently the maximum in the heat capacity should occur at about 74° K. Eucken and d'Or* have studied the heat capacity of NO between 130° K. and 180° K., and Fig. 7 shows that their results provide an excellent confirmation of this electronic contribution to the heat capacity.

The ground state of the oxygen molecule is a triplet $^3\Sigma$, but the separation between the three component states is appreciable only below 4° K., and is therefore undetectable by thermal or thermodynamic methods. At all ordinary temperatures we may therefore regard the $O_2$ molecules as in a degenerate state of weight 3, and there will be no electronic contribution to the heat capacity due to this multiplicity.

At very high temperatures an electronic contribution to the heat capacity is detectable due to the existence of a $^1\Delta$ state. The $^3\Sigma$ state has a weight 3

* Eucken and d'Or, *Gött. Nachr.* p. 107 (1932).

and the $^1\Delta$ state a weight 2. The electronic partition function is therefore

$$e(T) = 3+2e^{-\epsilon_1/kT}, \qquad (325,7)$$

where $\epsilon_1$ denotes the energy separation of the $^1\Delta$ level above the normal $^3\Sigma$ level. The observed value of $\epsilon_1$ is 0·97 electron volts, so that $\epsilon_1/k = 1{\cdot}13\times10^4$

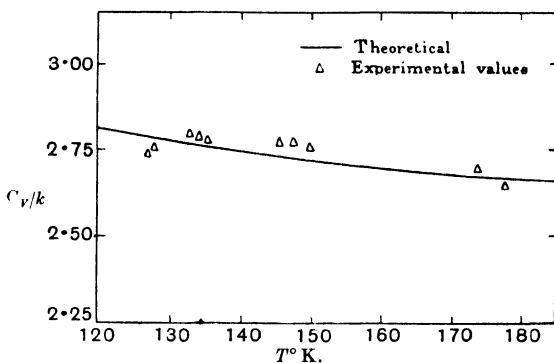



Fig. 7. The molecular heat capacity of NO at low temperatures.

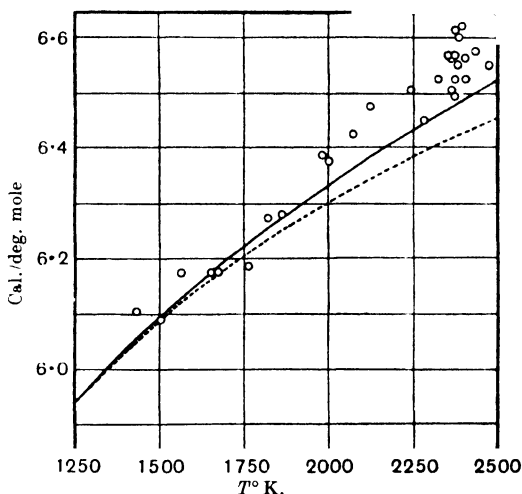



Fig. 8. Mean heat capacity (300° K. to $T^\circ$ K.) for oxygen: Spectroscopic curves: ———, $^1\Delta$ contribution included. - - - - -, $^1\Delta$ contribution excluded. Experimental points: ○, Lewis and von Elbe.

degrees. Formula (7) has been used by Johnston and Walker* to calculate the electronic contributions to the thermodynamic functions including the energy and the heat capacity. The experimental data,† which can be com-

* Johnston and Walker, *J. Am. Chem. Soc.* **57**, 682 (1935).

† B. Lewis and von Elbe, *J. Am. Chem. Soc.* **55**, 511 (1933).

pared with the theory, were obtained by exploding $O_3$ and measuring the temperature of the $O_2$ formed. This procedure leads directly to experimental values for the average heat capacity between room temperature (300° K.) and the temperature $T$ reached in the explosion. The calculated and observed values are compared in Fig. 8. Considering the difficulties of the experimental technique the agreement is not unsatisfactory.

**§ 326. Rotational degrees of freedom of rigid bodies.** Polyatomic molecules must be classified into two types, linear and non-linear, according as the equilibrium positions of all the nuclei do or do not lie on a straight line. For both types the rotational degrees of freedom are effectively classical. For the linear type there are only two classical rotational degrees of freedom, and the rotational-nuclear partition function takes the same classical form as for a diatomic molecule, and contains in the denominator a symmetry number $\sigma$ equal to 2 when the molecule has a centre of symmetry and otherwise equal to 1. Thus

$$r_n(T) = r(T)\frac{\Pi\rho}{\sigma} = \frac{8\pi^2 A kT}{h^2}\frac{\Pi\rho}{\sigma}, \tag{326, 1}$$

where $\Pi\rho$ denotes the product of the spin weights of the separate nuclei in the molecule.

For the non-linear type of rigid molecule, on the other hand, there are three classical rotational degrees of freedom, and we require the appropriate partition function. We shall consider only its classical form. The rotational motion of a rigid body with principal moments of inertia $A$, $B$, $C$ can be described by the three Eulerian* angles $\theta$, $\phi$, $\psi$ and their conjugate momenta $p_\theta$, $p_\phi$, $p_\psi$. The energy in Hamiltonian form is

$$\epsilon = \frac{1}{2A\sin^2\theta}\{(p_\phi - p_\psi\cos\theta)\cos\psi - p_\theta\sin\theta\sin\psi\}^2$$
$$+\frac{1}{2B\sin^2\theta}\{(p_\phi - p_\psi\cos\theta)\sin\psi + p_\theta\sin\theta\cos\psi\}^2 + \frac{1}{2C}p_\psi^2, \tag{326, 2}$$

and the rotational partition function, in the absence of symmetry, is

$$r(T) = \frac{1}{h^3}\int_0^\pi d\theta\int_0^{2\pi}d\phi\int_0^{2\pi}d\psi\int_{-\infty}^{+\infty}dp_\theta\int_{-\infty}^{+\infty}dp_\phi\int_{-\infty}^{+\infty}dp_\psi\, e^{-\epsilon/kT}. \tag{326, 3}$$

The energy can be expressed in the integrable form

$$\frac{1}{2}\left(\frac{\sin^2\psi}{A}+\frac{\cos^2\psi}{B}\right)\left\{p_\theta + \left(\frac{1}{B}-\frac{1}{A}\right)\frac{\sin\psi\cos\psi}{\sin\theta\left(\frac{\sin^2\psi}{A}+\frac{\cos^2\psi}{B}\right)}(p_\phi - p_\psi\cos\theta)\right\}^2$$
$$+\frac{1}{2AB\sin^2\theta}\frac{1}{\frac{\sin^2\psi}{A}+\frac{\cos^2\psi}{B}}(p_\phi - p_\psi\cos\theta)^2 + \frac{1}{2C}p_\psi^2. \tag{326, 4}$$

* See, for example, Routh, *Elementary Rigid Dynamics*, 1, chap v (Macmillan, 1905).

Integrating with respect to $p_\theta$, $p_\phi$, $p_\psi$ in that order we find

$$r(T) = \frac{(2\pi kT)^{\frac{3}{2}}(ABC)^{\frac{1}{2}}}{h^3}\int_0^\pi d\theta \int_0^{2\pi} d\phi \int_0^{2\pi} d\psi \sin\theta$$

$$= \frac{8\pi^2(2\pi kT)^{\frac{3}{2}}(ABC)^{\frac{1}{2}}}{h^3}. \qquad (326,5)$$

When molecules have symmetry, this can be taken care of by introducing into the denominator of the rotational-nuclear partition function a symmetry number $\sigma$, equal to the number of indistinguishable orientations of the molecule.* Thus

$$r_n(T) = \frac{8\pi^2(2\pi kT)^{\frac{3}{2}}(ABC)^{\frac{1}{2}}}{h^3}\frac{\Pi\rho}{\sigma}, \qquad (326,6)$$

where $\Pi\rho$ denotes the product of the spin weights of all nuclei in the molecule. The symmetry number is for example 2 for $OH_2$ (isosceles triangle), 3 for $NH_3$ (triangular pyramid), 4 for $C_2H_4$ (rectangle), 12 for $CH_4$ (regular tetrahedron) and 12 for $C_6H_6$ (regular hexagon).

**§ 327. Vibrational degrees of freedom of polyatomic molecules.** A polyatomic molecule has several normal modes, the number depending on the constitution of the molecule. A linear molecule composed of $a$ atoms has $3a-5$ normal vibrational modes, and a non-linear molecule with the same number of atoms has $3a-6$. Each mode $v$ has a characteristic temperature $\Theta_v$, related to the frequency $\nu_v$ by

$$k\Theta_v = h\nu_v. \qquad (327,1)$$

The partition function for such a mode regarded as a harmonic oscillation is

$$q_v(T) = (1-e^{-\Theta_v/T})^{-1}, \qquad (327,2)$$

and each mode will make a contribution to the free energy, to the energy, and to the heat capacity, of the same form as the vibrational contribution in a diatomic molecule.

It sometimes happens, when a molecule has elements of symmetry, that two or three modes have identical frequencies. Such a pair or triplet of modes is usually referred to as a degenerate mode of weight 2 or 3, and its contribution to each of the thermodynamic functions will be double or triple that of a non-degenerate mode of equal frequency.

**§ 328. Internal rotations of polyatomic molecules.** Large molecules are not necessarily rigid even when vibrational motions are ignored. In ethane, for example, the two $CH_3$ groups can rotate relative to each other. Until recently such a rotation was assumed to be effectively free. Let $\phi$

* For proof see Ludloff, *Zeit. Phys.* **57**, 227 (1929); or Mayer, Brunauer and Mayer, *J. Am. Chem. Soc.* **55**, 37 (1933).

denote the angle about the axis of rotation and $p_\phi$ its conjugate momentum. The partition function for such an internal free rotation would be

$$\frac{1}{h}\int_0^{2\pi} d\phi \int_{-\infty}^{+\infty} dp_\phi \, e^{-\frac{1}{2}p_\phi^2/IkT} = \frac{2\pi(2\pi IkT)^{\frac{1}{2}}}{h}; \qquad (328, 1)$$

$I$ is here the reduced moment of inertia defined by

$$I = I_1 I_2/(I_1 + I_2), \qquad (328, 2)$$

where $I_1$, $I_2$ are the moments of inertia, about the axis of rotation, of the two parts of the molecules rotating relative to each other. When we use (1) as a factor in the complete partition function of the molecule, we must take care of symmetry requirements by inserting a factor $1/\sigma^{(i)}$, where $\sigma^{(i)}$ is an internal symmetry number equal to the number of indistinguishable relative configurations of the two parts of the molecule; for ethane $\sigma^{(i)}$ would be 3.

An internal rotation of this kind is never really free. There will be maxima and minima of potential energy according to the relative configurations defined by the angle $\phi$. This potential energy $u$ may be represented semi-quantitatively by a function of the form

$$u = \tfrac{1}{2}u_0\{1 - \cos\sigma^{(i)}\phi\} = u_0 \sin^2(\tfrac{1}{2}\sigma^{(i)}\phi), \qquad (328, 3)$$

where we have taken the minima of potential energy as zero and the maxima as $u_0$. We have assumed that all the minima are equal and all the maxima likewise; the number of each must then be $\sigma^{(i)}$. If now $u_0 \ll kT$, the internal rotation will be effectively free and the partition function (1), divided by $\sigma^{(i)}$, will be a good approximation. In the opposite case, $u_0 \gg kT$, only small values of $u$ will contribute appreciably to the partition function. We may then replace (3) by the approximation

$$u = u_0(\tfrac{1}{2}\sigma^{(i)}\phi)^2. \qquad (328, 4)$$

This form for the potential energy is that of a harmonic oscillator of frequency $\nu_v$ and characteristic temperature $\Theta_v$ given by

$$\nu_v = k\Theta_v/h = \sigma^{(i)}(u_0/2I)^{\frac{1}{2}}/2\pi, \qquad (328, 5)$$

and the partition function will have the usual form for a harmonic oscillator with this value of $\Theta_v$. When $u_0$ is comparable to $kT$, the motion is of an intermediate and more complicated kind.* Explicit formulae for the partition function cannot be obtained, but its value can be computed as a function of $u_0/kT$ and $h\sigma^{(i)}/I^{\frac{1}{2}}u_0^{\frac{1}{2}}$. Such computations have been carried out by Pitzer,† who gives tables for the contributions of a restricted internal rotation to the several thermodynamic functions.

Unfortunately it has not yet proved possible to calculate *a priori* the

* Nielsen, *Phys. Rev.* **40**, 445 (1932); Teller and **Weigert**, *Nachr. Ges. Wiss. Göttingen, Math. Physik. Klasse*, p. 218 (1933).

† Pitzer, *J. Chem. Phys.* **5**, 469 (1937).

magnitude of the energy barrier which impedes rotation, though a first attack on the problem for ethane has been made by Penney.* Nor are optical data of much help, as the internal rotation does not give rise to a fundamental frequency in either the infra-red or the Raman spectrum. One can therefore only estimate its value *a posteriori* by examining what value will be in agreement with experimental data such as heat capacities. Such a comparison is made at the end of § 330, and leads to the conclusion that for ethane the energy barrier is slightly over 3 k.cal./mole. The corresponding value of $u_0/k$ is about 1500°. It is therefore clear that at ordinary temperatures the rotation is far from free.† This fact does not conflict‡ with the organic chemist's postulation of "free rotation", which only means that equilibrium is established rapidly between the various relative configurations. A potential barrier of 3 k.cal./mole is, as we shall see in Chapter XII, certainly low enough to allow this. We shall not give formulae for molecules with internal impeded rotations, but it should be remembered that, when such are present, the appropriate partition function occurs in place of one or more of the vibrational partition functions.

§ 329. **Final formulae for polyatomic molecules.** By combining the various types of partition functions derived above, we obtain the following final partition function for polyatomic molecules:

*Linear molecules:*

$$f(T) = \frac{(2\pi m kT)^{\frac{3}{2}} V}{h^3} \frac{8\pi^2 A kT}{h^2} \Pi_v (1 - e^{-\Theta_i/T})^{-1} \varpi_0 \frac{\Pi\rho}{\sigma}. \qquad (329, 1)$$

*Non-linear molecules:*

$$f(T) = \frac{(2\pi m kT)^{\frac{3}{2}} V}{h^3} \frac{8\pi^2 (2\pi kT)^{\frac{3}{2}} (ABC)^{\frac{1}{2}}}{h^3} \Pi_v (1 - e^{-\Theta_i/T})^{-1} \varpi_0 \frac{\Pi\rho}{\sigma}. \quad (329, 2)$$

In these formulae $\sigma$, the symmetry number, is equal to the number of indistinguishable configurations of the rotating molecule supposed rigid; the product $\Pi_v$ extends over all the vibrational modes; $\varpi_0$ is the statistical weight of the lowest electronic level; $\Pi\rho$ denotes the product of the spin weights of all the nuclei in the molecule. If one part of the molecule can rotate freely with respect to the rest, there will be a rotational factor like (328, 1) in place of one of the vibrational factors $(1 - e^{-\Theta_i/T})^{-1}$. We shall not consider this possibility any further. If electronic levels other than the lowest are important, and possess substantially unaltered values of the moments of inertia and other molecular constants, the factor $\varpi_0$ must be

* Penney, *Proc. Roy. Soc.* A, **144**, 166 (1934).

† Recent measurements of heat capacity on dimethylacetylene ($CH_3C{\equiv}C.CH_3$) indicate that in this molecule the rotation of the two $CH_3$ groups relative to each other is effectively free. See Crawford and Rice, *J. Chem. Phys.* **7**, 437 (1939).

‡ Cf. Wagner, *Zeit. Physikal. Chem.* B, **14**, 166 (1931).

replaced by $e(T) = \upsilon_0 + \Sigma_r \upsilon_r e^{-\epsilon_r/kT}$, where $\epsilon_r$ is the energy of the $r$th electronic state. If these other electronic levels have seriously different values of the molecular constants, no compact formula can be given, but formulae of the preceding type can be used for the contributions of each electronic level, $\upsilon_0$ being replaced by $\upsilon_1 e^{-\epsilon_1/kT}$, $\upsilon_2 e^{-\epsilon_2/kT}$, ....

For the free energy we have:

*Linear molecules:*

$$F = NkT\left\{\log\frac{N}{V}-1\right\} - \tfrac{5}{2}NkT\log T + NkT\,\Sigma_v \log(1-e^{-\Theta_v/T})$$
$$-NkT\log\left\{\frac{(2\pi mk)^{\frac{3}{2}}}{h^3}\,\frac{8\pi^2 Ak}{h^2}\,\upsilon_0\,\frac{\Pi\rho}{\sigma}\right\}. \qquad (329,3)$$

*Non-linear molecules:*

$$F = NkT\left\{\log\frac{N}{V}-1\right\} - 3NkT\log T + NkT\,\Sigma_v \log(1-e^{-\Theta_v/T})$$
$$-NkT\log\left\{\frac{(2\pi mk)^{\frac{3}{2}}}{h^3}\,\frac{8\pi^2(2\pi k)^{\frac{3}{2}}(ABC)^{\frac{1}{2}}}{h^3}\,\upsilon_0\,\frac{\Pi\rho}{\sigma}\right\}. \qquad (329,4)$$

For the energy we have:

*Linear molecules:*

$$E = -T^2\frac{\partial(F/T)}{\partial T} = \tfrac{5}{2}NkT + NkT\,\Sigma_v\frac{\Theta_v/T}{e^{\Theta_v/T}-1}. \qquad (329,5)$$

*Non-linear molecules:*

$$E = -T^2\frac{\partial(F/T)}{\partial T} = 3NkT + NkT\,\Sigma_v\frac{\Theta_v/T}{e^{\Theta_v/T}-1}. \qquad (329,6)$$

For the partial potentials we have:

*Linear molecules:*

$$\mu = \left(\frac{\partial F}{\partial N}\right)_{T,V} = kT\log\frac{N}{V} - \tfrac{5}{2}kT\log T + kT\,\Sigma_v\log(1-e^{-\Theta_v/T})$$
$$-kT\log\left\{\frac{(2\pi mk)^{\frac{3}{2}}}{h^3}\,\frac{8\pi^2 Ak}{h^2}\,\upsilon_0\,\frac{\Pi\rho}{\sigma}\right\},$$
$$= kT\log p - \tfrac{7}{2}kT\log T + kT\,\Sigma_v\log(1-e^{-\Theta_v/T})$$
$$-kT\log\left\{\frac{(2\pi m)^{\frac{3}{2}}k^{\frac{5}{2}}}{h^3}\,\frac{8\pi^2 Ak}{h^2}\,\upsilon_0\,\frac{\Pi\rho}{\sigma}\right\}. \qquad (329,7)$$

*Non-linear molecules:*

$$\mu = kT\log\frac{N}{V} - 3kT\log T + kT\,\Sigma_v\log(1-e^{-\Theta_v/T})$$
$$-kT\log\left\{\frac{(2\pi mk)^{\frac{3}{2}}}{h^3}\,\frac{8\pi^2(2\pi k)^{\frac{3}{2}}(ABC)^{\frac{1}{2}}}{h^3}\,\upsilon_0\,\frac{\Pi\rho}{\sigma}\right\},$$
$$= kT\log p - 4kT\log T + kT\,\Sigma_v\log(1-e^{-\Theta_v/T})$$
$$-kT\log\left\{\frac{(2\pi m)^{\frac{3}{2}}k^{\frac{5}{2}}}{h^3}\,\frac{8\pi^2(2\pi k)^{\frac{3}{2}}(ABC)^{\frac{1}{2}}}{h^3}\,\upsilon_0\,\frac{\Pi\rho}{\sigma}\right\}. \qquad (329,8)$$

For the molecular heat capacities we have:

*Linear molecules:*

$$C_V/k = \frac{1}{Nk}\left(\frac{\partial E}{\partial T}\right)_V = \frac{5}{2} + \Sigma_v \frac{(\frac{1}{2}\Theta_v/T)^2}{\sinh^2(\frac{1}{2}\Theta_v/T)}. \qquad (329, 9)$$

*Non-linear molecules:*

$$C_V/k = \frac{1}{Nk}\left(\frac{\partial E}{\partial T}\right)_V = 3 + \Sigma_v \frac{(\frac{1}{2}\Theta_v/T)^2}{\sinh^2(\frac{1}{2}\Theta_v/T)}. \qquad (329, 10)$$

From the form of (9) and (10) it is clear that any mode for which $\Theta_v \ll T$ will contribute $k$ to $C_V$, while any mode for which $\Theta_v \gg T$ will contribute nothing to $C_V$. One therefore requires an accurate value of $\Theta_v$ only when $\Theta_v$ is comparable to $T$. At ordinary temperatures such modes are those with wave numbers between 100 cm.$^{-1}$ and 2000 cm.$^{-1}$, but modes with wave numbers less than 300 cm.$^{-1}$ are rare.

**§ 330. Application to heat capacities of polyatomic molecules.** For comparison of the theoretical formulae with experimental values it is necessary to know the vibrational frequencies of the various normal modes. These are now known with reasonable certainty for more than fifty polyatomic molecules. When these frequencies are known, it is almost certain that the values of the heat capacities calculated from the spectroscopic data are more accurate than any measured values. It is therefore superfluous to compare with theory any but the most reliable experimental data.*

To illustrate the variety in the normal modes of polyatomic molecules, we have collected in Tables 5, 6, 7 the spectroscopic data† for a selection of important simple molecules of various common shapes. For each molecule we give a list of the normal modes, specifying, for the benefit of spectroscopists, their symmetry class as well as their frequencies $\Theta_v$ expressed in degrees. We shall not explain the meaning of symmetry class, nor the symbols used to describe it, but will merely mention that the symmetry class determines the optical properties of the modes, in particular whether they can occur as fundamentals in the Raman or in the infra-red spectra.‡ We have also included the calculated contributions of the several modes to the heat capacity at one selected temperature and the resultant heat capacity at this temperature. When a fairly reliable experimental value is available for the heat capacity, the temperature for the calculation has been

* A useful and interesting review of this field has been given by Bartholomé, *Zeit. Elektrochem.* **42**, 341 (1936).

† We are indebted to Mr C. R. Bailey, who is compiling a survey of spectroscopic data, Raman and infra-red, for his unpublished tables, from which we have taken our values for the frequency of the normal modes. Values given by Sponer, *Molekülspektren* (Springer, 1935), in most cases differ insignificantly from those selected by Bailey.

‡ See Placzek, *Handb. d. Radiologie*.

## TABLE 5

*Vibrational contributions to heat capacities of linear polyatomic molecules at temperatures selected for comparison with experiment*

$$C_P/k = \tfrac{7}{2} + C^{\text{vib}}/k$$

| Formula and temp. | | Normal modes | | | | | $C^{\text{vib}}/k$ calc. | $C_P/k$ calc. | $C_P/k$ exp. |
|---|---|---|---|---|---|---|---|---|---|
| OCO | Symmetry class | $A_{1g}$ | $A_{2u}$ | $E_{1u}$ | | | | | |
| | Number of modes | 1 | 1 | 2 | | | | | |
| | $\Theta_v/100$ | 18·9 | 33·6 | 9·54 | | | | | |
| $T = 312°$ K. | Contribution to $C/k$ | 0·086 | — | 2 × 0·483 | | | 1·05 | 4·55 | 4·53 |
| NNO | Symmetry class | | | | | | | | |
| | Number of modes | 1 | 1 | 2 | | | | | |
| | $\Theta_v/100$ | 18·4 | 32·0 | 8·5 | | | | | |
| $T = 314°$ K. | Contribution to $C/k$ | 0·100 | 0·004 | 2 × 0·562 | | | 1·23 | 4·73 | 4·75 |
| HCCH | Symmetry class | $A_g$ | $A_g$ | $A_u$ | $E_g$ | $E_u$ | | | |
| | Number of modes | 1 | 1 | 1 | 2 | 2 | | | |
| | $\Theta_v/100$ | 28·2 | 48·3 | 46·9 | 9·11 | 10·44 | | | |
| $T = 291$ K. | Contribution to $C/k$ | — | — | — | 2 × 0·465 | 2 × 0·377 | 1·69 | 5·19 | 5·20 |

Experimental values of $C_P$ for $C_2H_2$ taken from Heuse, *Ann d Phys* **59**, 86 (1919) For other molecules see references at foot of Table 8.

TABLE 6

*Vibrational contributions to heat capacities of symmetrical top molecules at temperatures selected for comparison with experiment*

$C_p/k = 4 + C^{\text{vib}}/k$

| Formula, shape and temp. | Normal modes | | | | | | | $C^{\text{vib}}/k$ calc. | $C_p/k$ calc. | $C_p/k$ exp. |
|---|---|---|---|---|---|---|---|---|---|---|
| $BF_3$ | Symmetry class | $A_1'$ | $A_2''$ | $E'$ | $E'$ | | | | | |
| Plane equi- | Number of modes | 1 | 1 | 2 | 2 | | | | | |
| lateral | $\Theta_v/100$ | 12·7 | 9·95 | 20·7 | 6·31 | | | | | |
| triangle | | | | | | | | | | |
| $T = 278°$ K. | Contribution to $C/k$ | 0·221 | 0·378 | 2 × 0·033 | 2 × 0·662 | | | 1·99 | 5·99 | 5·89 |
| $T = 189°$ K. | Contribution to $C/k$ | 0·055 | 0·145 | 2 × 0·002 | 2 × 0·425 | | | 1·05 | 5·05 | 5·04 |
| $NH_3$ | Symmetry class | $A_1$ | $A_1$ | $E_1$ | $E_1$ | | | | | |
| Trigonal | Number of modes | 1 | 1 | 2 | 2 | | | | | |
| pyramid | $\Theta_v/100$ | 47·8 | 13·6 | 48·8 | 23·3 | | | | | |
| $T = 300°$ K. | Contribution to $C/k$ | — | 0·225 | — | 2 × 0·026 | | | 0·28 | 4·28 | 4·29 |
| $CH_4$ | Symmetry class | $A_1$ | $E$ | $T_2$ | $T_2$ | | | | | |
| Regular | Number of modes | 1 | 2 | 3 | 3 | | | | | |
| tetrahedron | $\Theta_v/100$ | 41·7 | 21·8 | 43·2 | 18·7 | | | | | |
| $T = 300°$ K. | Contribution to $C/k$ | — | 2 × 0·037 | — | 3 × 0·077 | | | 0·30 | 4·30 | 4·31 |
| $CHCl_3$ | Symmetry class | $A$ | $A$ | $A$ | $E$ | $E$ | $E$ | | | |
| Tetrahedron | Number of modes | 1 | 1 | 1 | 2 | 2 | 2 | | | |
| with trigonal | $\Theta_v/100$ | 5·23 | 9·38 | 43·3 | 3·74 | 10·90 | 17·45 | | | |
| symmetry | | | | | | | | | | |
| $T = 300°$ K. | Contribution to $C/k$ | 0·783 | 0·469 | — | 2 × 0·883 | 2 × 0·370 | 2 × 0·100 | 3·96 | 7·96 | — |

Experimental value for $BF_3$ taken from Millar, *J. Am. Chem. Soc.* **45**, 874 (1923). For other molecules see references at foot of Table 8.

TABLE 7

*Vibrational contributions to heat capacities of asymmetrical top molecules at selected temperatures*

$c_p/k = 4 + c^{vib}/k$

| Formula, shape and temp. | Normal modes | | | | | | | $c^{vib}/k$ calc. | $c_p/k$ calc. |
|---|---|---|---|---|---|---|---|---|---|
| $H\,{}_{O}\,H$ | Symmetry class | $A_1$ | $A_1$ | $B_1$ | | | | | |
| Isosceles | Number of modes | 1 | 1 | 1 | | | | | |
| triangle | $\Theta_v/100$ | 22·9 | 51·6 | 53·6 | | | | | |
| $T = 500°$ K. | Contribution to $c/k$ | 0·219 | 0·003 | 0·002 | | | | 0·22 | 4·22 |
| $O\,{}_{N}\,Cl$ | Symmetry class | $A_1$ | $A_1$ | $A_1$ | | | | | |
| Scalene | Number of modes | 1 | 1 | 1 | | | | | |
| triangle | $\Theta_v/100$ | 9·07 | 13·2 | 26·2 | | | | | |
| $T = 300°$ K. | Contribution to $c/k$ | 0·488 | 0·243 | 0·008 | | | | 0·74 | 4 74 |
| $H_{H}CO$ | Symmetry class | $A_1$ | $A_1$ | $A_1$ | $B_1$ | $B_2$ | $B_1$ | | |
| Plane | Number of modes | 1 | 1 | 1 | 1 | 1 | 1 | | |
| isosceles | $\Theta_v/100$ | 39·8 | 25·0 | 21·5 | 40·0 | 18·3 | 16 7 | | |
| triangle | | | | | | | | | |
| $T = 300°$ K. | Contribution to $c/k$ | — | 0·017 | 0·040 | — | 0 084 | 0 120 | 0 26 | 4·26 |

selected so as to allow comparison with experiment. In most cases the agreement is satisfactory.

We turn now to a more detailed discussion of those few molecules, for which reliable experimental values of the heat capacity are available over an extended range of temperatures. Data obtained from measurements of the velocity of sound are, for reasons already given in our discussion of diatomic molecules, not suitable for comparison with the theory The data obtained by other reliable methods for the linear molecules $CO_2$, $N_2O$ and for the non-linear molecules $NH_3$, $CH_4$ are collected in Table 8. It will be seen that the agreement between theory and experiment is excellent.

Reliable experimental data are also available for ethylene and ethane, and these molecules merit special discussion. The normal modes of ethylene $H_2C.CH_2$ are given in Table 9. We have used the recent assignment of Bonner;* earlier alternative assignments do not differ significantly from that of Bonner, except in the case of the $B_{3g}$ mode, which has so far been observed only as a combination frequency in the Raman spectrum. From the nature of this mode its wave number would be expected not to differ

* Bonner, *J Am Chem. Soc.* **58**, 34 (1936).

TABLE 8

*Heat capacities of polyatomic molecules at high temperatures*

$$\frac{C_p}{k} = \frac{C_p^0}{k} + \Sigma_v \left\{ \frac{\frac{1}{2}\Theta_v/T}{\sinh(\frac{1}{2}\Theta_v/T)} \right\}^2,$$

*where* $C_p^0/k = \frac{7}{2}$ *for linear molecules, and* $C_p^0/k = 4$ *for non-linear molecules*

| Substance and values of $\Theta_v/100$ | $T$ °K. | $C_p/k$ calc. | $C_p/k$ obs. | Observers |
|---|---|---|---|---|
| $CO_2$ | | | | |
| 9·54 | 198 | 3·89 | 3·92 | Heuse |
| 9·54 | 271 | 4·32 | 4·29 | E.L. |
| 18·9 | 293 | 4·46 | 4·44 | Heuse |
| 33·6 | 293 | 4·46 | 4·42 | E.L. |
| | 308 | 4·53 | 4·52 | Henry |
| | 312 | 4·55 | 4·61 | Henry |
| | 323 | 4·61 | 4·64 | Henry |
| | 331 | 4·65 | 4·70 | Henry |
| | 358 | 4·79 | 4·80 | E.L. |
| | 430 | 5·10 | 5·12 | E.L. |
| | 488 | 5·34 | 5 39 | E.L. |
| | 493 | 5·36 | 5·35 | Henry |
| | 648 | 5·85 | 5·76 | Henry |
| | 683 | 5·92 | 5·81 | Henry |
| | 690 | 5·95 | 6·00 | E.M. |
| | 832 | 6·24 | 6·16 | Henry |
| | 871 | 6·30 | 6·45 | E.M. |
| | 969 | 6·49 | 6·33 | Henry |
| | 1054 | 6·60 | 6·50 | Henry |
| | 1157 | 6·71 | 6·53 | Henry |

| Substance and values of $\Theta_v/100$ | $T$ °K. | $C_p/k$ calc. | $C_p/k$ obs. | Observers |
|---|---|---|---|---|
| $N_2O$ | | | | |
| 8·50 | 203 | 4·06 | 4·10 | Heuse |
| 8·50 | 243 | 4·31 | 4·35 | Heuse |
| 18·4 | 272 | 4·50 | 4·49 | E.L. |
| 32·0 | 287 | 4·56 | 4·61 | E.L. |
| | 293 | 4·61 | 4·61 | Heuse |
| | 314 | 4·71 | 4·75 | Henry |
| | 390 | 5·08 | 5·05 | E.L. |
| | 467 | 5·49 | 5·46 | Henry |
| | 625 | 5·89 | 5·90 | Henry |
| | 733 | 6·15 | 6·15 | Henry |
| $NH_3$ | | | | |
| 13·6 | 243 | 4·12 | 4·14 | O.S. |
| 23·3 | 273 | 4·19 | 4·22 | O.S. |
| 23·3 | 303 | 4·29 | 4·31 | O.S. |
| 47·8 | 343 | 4·37 | 4·45 | O.S. |
| 48·8 | 383 | 4·56 | 4·60 | O.S. |
| 48·8 | 423 | 4·70 | 4·75 | O.S. |
| | 582 | 5·31 | 5·2 | Haber |
| | 695 | 5·72 | 5·5 | Haber |
| | 796 | 6·06 | 5·9 | Haber |
| $CH_4$ | | | | |
| 18·7 | 193 | 4·01 | 4·02 | Heuse |
| 18·7 | 218 | 4·04 | 4·04 | Heuse |
| 18·7 | 243 | 4·10 | 4·07 | Heuse |
| 21·8 | 278 | 4·21 | 4·225 | Heuse |
| 21·8 | 288 | 4·26 | 4·27 | Heuse |
| Four | 298 | 4·30 | 4·30 | E.L. |
| others | 398 | 4·97 | 5·08 | E.L. |
| above 40 | 481 | 5·55 | 5·64 | E.L. |

*References to Table 8*

Heuse, *Ann. d. Phys* **59**, 86 (1919).
E L.: Eucken and von Lüde, *Zeit. Physikal. Chem.* B, **5**, 413 (1929).
E.M.: Eucken and Mucke, *Zeit. Physikal. Chem.* B, **18**, 184 (1932).
Henry: Unpublished data privately communicated.
O.S.: Osborne, Stimson, Sligh and Cragoe, *Refrig. Eng.* **10**, 145 (1923); *Phys. Ber.* **5**, 271 (1924). Authors' smoothed values.
Haber: Haber and Tamaru, *Zeit. Elektrochem.* **21**, 228 (1915).

TABLE 9

*Normal modes of ethylene as assigned by Bonner*

| Symmetry class | Reference* symbol | Wave number cm.$^{-1}$ | $\Theta_v/10^2$ deg. |
|---|---|---|---|
| $A_{1g}$ | $\nu_2$ | 3019 | 43·3 |
| | $\nu_4$ | 1623 | 23·25 |
| | $\nu_8$ | 1342 | 19·3 |
| $A_{1u}$ | $\nu_7$ | ? | ? |
| $B_{1u}$ | $\nu_1$ | 2988 | 42·8 |
| | $\nu_3$ | 1444 | 20·7 |
| $B_{2g}$ | $\nu_6$ | 3069 | 44·0 |
| | $\nu_{10}$ | 950 | 13·6 |
| $B_{2u}$ | $\nu_{11}$ | 940 | 13·45 |
| $B_{3g}$ | $\nu_{12}$ | 1100 | 15·75 |
| $B_{3u}$ | $\nu_5$ | 3107 | 44·5 |
| | $\nu_9$ | 950 | 13·6 |

* These are the symbols used by Sutherland.

seriously from the value assigned by Bonner. There remains the $A_{1u}$ mode, a twisting of one $CH_2$ group relative to the other. This mode is completely inactive both in the Raman and infra-red spectra. The best one can do is to investigate whether one can assign to this twisting frequency a value which will fit the observed thermodynamic properties. The value which we have assumed for this purpose is 900 cm.$^{-1}$, which corresponds to $\Theta_v = 12{\cdot}9 \times 10^2$ deg. The comparison of the experimental data of Heuse and of Eucken and Parts with the values calculated with this assumed value for the $A_{1u}$ mode is given in Table 10. The agreement is all that could be desired.

For ethane $CH_3.CH_3$, as for ethylene, most of, but not all, the vibration frequencies have been determined unambiguously from observations of the infra-red and Raman spectra. The eighteen normal modes split into six non-degenerate modes and twelve doubly degenerate modes (pairs of modes of equal frequencies). In Table 11 are given the most reliable assignment of frequencies as determined from observations of the infra-red and Raman spectrum by Crawford, Avery and Linnett.† There have been several previous assignments, but they are all in essential agreement‡ except with respect to the $E''$ frequency 1120 cm.$^{-1}$. This frequency does not occur as a fundamental either in the infra-red or in the Raman spectrum, and is conveniently referred to as the uncertain frequency. The $A_1''$ mode to which no frequency is assigned in the table consists of a twisting of one $CH_3$ relative to the other $CH_3$. In the past it was believed that this mode was one of free rotation, in which case it should contribute $\frac{1}{2}k$ to the molecular heat capacity.

† Crawford, Avery and Linnett, *J. Chem. Phys.* **6**, 682 (1938).

‡ See, however, a recent note by Barker, *J. Chem. Phys.* **7**, 277 (1939).

TABLE 10

*Heat capacity of ethylene*

Twisting frequency assumed to be 900 cm.$^{-1}$ or $12\cdot9 \times 10^2$ deg.

| $T°$ K. | Contribution to $C/k$ of seventeen known frequencies | Contribution to $C/k$ of twisting frequency | $C_P/k$ calc. | $C_P/k$ obs. | Observers |
|---|---|---|---|---|---|
| 179 | 0·101 | 0·038 | 4·14 | 4·175 | E.P. |
| 182 | 0·155 | 0·042 | 4·16 | 4·17 | Heuse |
| 193 | 0·159 | 0·057 | 4·22 | 4·25 | E.P. |
| 205 | 0·219 | 0·074 | 4·29 | 4·30 | Heuse |
| 211 | 0·247 | 0·083 | 4·33 | 4·37 | E.P. |
| 231 | 0·378 | 0·119 | 4·50 | 4·53 | E.P. |
| 237 | 0·419 | 0·129 | 4·55 | 4·54 | Heuse |
| 251 | 0·534 | 0·156 | 4·69 | 4·70 | E.P. |
| 272 | 0·708 | 0·200 | 4·91 | 4·94 | E.P. |
| 291 | 0·882 | 0·239 | 5·12 | 5·11 | Heuse |
| 293·5 | 0·909 | 0·245 | 5·15 | 5·16 | E.P. |
| 368 | 1·676 | 0·393 | 6·07 | 5·99 | E.P. |
| 464 | 2·670 | 0 543 | 7·21 | 7·13 | E.P. |

*References to Table* 10

Heuse, *Ann. d. Phys.* **59**, 86 (1919).
E.P.: Eucken and Parts, *Zeit. Physikal. Chem.* B, **20**, 184 (1933).

TABLE 11

*Normal modes of ethane as assigned by Crawford, Avery and Linnett*

| Non-degenerate modes | | | Doubly degenerate modes | | |
|---|---|---|---|---|---|
| Symmetry class* | Wave number cm.$^{-1}$ | $\Theta_v/10^2$ deg. | Symmetry class* | Wave number cm.$^{-1}$ | $\Theta_v/10^2$ deg. |
| $A_1'$ | 993 | 14·20 | $E'$ | 827 | 11·84 |
| | 1375 | 19·6 | | 1480 | 21·2 |
| | 2927 | 41·9 | | 2980 | 42·6 |
| $A_2''$ | 1380 | 19·8 | $E''$ | 1120 | 16·0 |
| | 2926 | 41·9 | | 1460 | 20·9 |
| $A_1''$ | ? | | | 2970 | 42·5 |

* These symmetry classes assume a molecule with a point group $D_{3h}$. There are other alternative possibilities.

When this assumption is made it is found that the experimental heat capacities at ordinary and high temperatures can be made to agree with the calculated values only by assigning a value about 710 cm.$^{-1}$ instead of 1120 cm.$^{-1}$ to the uncertain frequency. It was, however, pointed out by

Wagner* that the value of the heat capacity at 191° K. found by Heuse was higher than would be expected if there were an internal free rotation. He proposed the alternative of a restricted rotation, which should behave as a vibration at low temperatures, and as an effectively free rotation at very high temperatures. The crucial test is provided by measurements of heat capacity at lower temperatures. These have recently been made by several workers†, and they show conclusively that the rotation is far from free. The heat capacity data over the whole experimental range from 100° K. to 370° K. are brought into excellent agreement with values calculated from the frequencies given in Table 11, if one assumes the $A_1''$ mode to be a restricted rotation with a potential energy of the form of (328, 3) with $u_0/k = 1570$ deg. The extent of this agreement|| is shown in Fig. 9. The

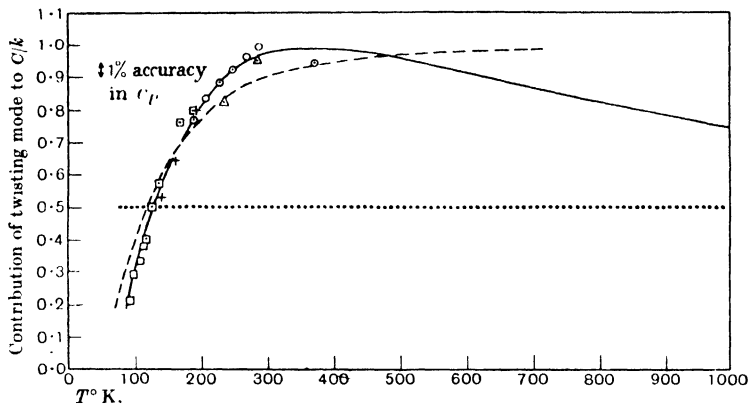



Fig. 9. Contribution to the molecular heat capacity of the twisting mode in ethane.

△ Heuse, *Ann. d. Phys.* **59**, 86 (1919).
⊙ Eucken and Parts, *Zeit. Physikal. Chem.* B, **20**, 184 (1933).
+ Kistiakowsky and Nazmi, *J. Chem. Phys.* **6**, 18 (1938).
□ Hunsmann, *Zeit. Physikal. Chem.* B, **39**, 23 (1938).
——— Restricted rotation with $u_0/k = 1570$.
.......... Free rotation.
----- Harmonic oscillation with $\Theta = 350$.

theoretical contribution of the restricted rotation has been taken from the tables constructed by Pitzer.‡ The approximate value $u_0/k = 1570$ deg. for the height of the restricting energy has been estimated and confirmed by several authors.§ This analysis of the heat capacities provides confirmation

* Wagner, *Zeit. Physikal. Chem.* B, **14**, 166 (1931).

† Kistiakowsky and Nazmi, *J. Chem. Phys.* **6**, 18 (1938); Hunsmann, *Zeit. Physikal. Chem*, B, **39**, 23 (1938).

‡ Pitzer, *J. Chem. Phys.* **5**, 469 (1937).

|| See footnote on p. 125.

§ Kemp and Pitzer, *J. Chem. Phys.* **4**, 749 (1936); *J. Am. Chem. Soc.* **59**, 276 (1937); Howard, *J. Chem. Phys.* **5**, 451 (1937); Kistiakowsky and Nazmi, *J. Chem. Phys.* **6**, 18 (1938).

of the approximate correctness of the value 1120 cm.$^{-1}$ assigned to the uncertain frequency. Quite recently Karweil* claimed to have spectroscopic evidence for the value 740 cm.$^{-1}$ for this frequency, but he has since† agreed to the correctness of a value near 1120 cm.$^{-1}$.

Summing up this survey we may say that, when all the frequencies of the normal modes are known and the heat capacities have been measured in such a manner as to ensure that the true values are obtained, there is in all cases excellent agreement between theory and experiment. The agreement is in fact so good that we are justified in placing complete confidence in calculated values at still higher temperatures where experimental data are difficult to obtain. To obtain completely accurate calculated values one would have to take account of anharmonicities. We have also seen how, when there is a gap in the observed frequencies, this gap can be filled by a proper analysis of the experimental data for the heat capacities, provided that these data extend over a sufficient range of temperatures. This procedure, which we have already described in detail for $C_2H_4$ and $C_2H_6$, has been used by Eucken and Bertram‡ for the molecules $SeF_6$, $TeF_6$, $CF_2Cl_2$, $C_2H_2$ and $C_2N_2$.

§ 331. **Polyatomic molecules at very low temperatures.** The only polyatomic molecules whose rotations might conceivably cease to be classical in accessible temperature ranges are those, such as $CH_4$, $NH_3$ and $OH_2$, containing only one atom other than hydrogen. Low temperature observations on the gas are practicable only for $CH_4$ (methane) and we shall therefore confine our discussion to this molecule.

Owing to the identity of the four H nuclei, the rotational-nuclear states of this isotropic rotator will break up into three non-combining groups.§ These three groups consist of a nuclear spin quintet with spin weight 5; three nuclear spin triplets each with a nuclear spin weight 3; two nuclear spin singlets each with a nuclear spin weight 1. Methane will therefore behave as a mixture of three forms, whose rotational-nuclear partition functions we shall denote by ${}^5r_n(T)$, ${}^3r_n(T)$ and ${}^1r_n(T)$ respectively. We can write formally

$$ {}^5r_n(T) = \quad 5\,.\,{}^5r(T), \qquad (331,1)$$

$$ {}^3r_n(T) = 3\times 3\,.\,{}^3r(T), \qquad (331,2)$$

$$ {}^1r_n(T) = 2\times 1\,.\,{}^1r(T), \qquad (331,3)$$

the displayed factors 5, 3, 1 being the nuclear spin weights.

* Karweil, *Zeit. Physikal. Chem.* B, **39**, 1 (1938).
† Karweil and Schäfer, *Zeit. Physikal. Chem.* B, **40**, 382 (1938).
‡ Eucken and Bertram, *Zeit. Physikal. Chem.* B, **31**, 363 (1936).
§ Hund, *Zeit. Phys.* **42**, 93 (1927); **43**, 778 (1927).

To determine ${}^5r(T)$, ${}^3r(T)$ and ${}^1r(T)$ one requires to know which rotational states are accessible, according to symmetry requirements, for molecules in the three groups of nuclear spin states. An elaborate analysis is required* and we shall merely quote the result. It can be shown that

$$ {}^5r(T) = \sum_{j=0}^{\infty} \{\tfrac{1}{12}(2j+1) + {}^5\alpha_j\}(2j+1)\, e^{-j(j+1)\Theta_r/T}, \qquad (331,4)$$

$$ {}^3r(T) = \sum_{j=0}^{\infty} \{\tfrac{1}{12}(2j+1) + {}^3\alpha_j\}(2j+1)\, e^{-j(j+1)\Theta_r/T}, \qquad (331,5)$$

$$ {}^1r(T) = \sum_{j=0}^{\infty} \{\tfrac{1}{12}(2j+1) + {}^1\alpha_j\}(2j+1)\, e^{-j(j+1)\Theta_r/T}, \qquad (331,6)$$

where

$$\Theta_r = h^2/8\pi^2 Ak, \qquad (331,7)$$

and ${}^5\alpha_j$, ${}^3\alpha_j$, ${}^1\alpha_j$ are numbers with values between $-1$ and $+1$, varying from one rotational state to another and also depending on the vibrational state. For any specified vibrational state and in particular for the zeroth vibrational state, the only one occupied appreciably at low temperatures, the value of each of the quantities ${}^5\alpha_j$, ${}^3\alpha_j$, ${}^1\alpha_j$ fluctuates in such a manner that its average over any set of six successive values of $j$ is zero. At sufficiently high temperatures one may replace the accurate values of ${}^5r(T)$, ${}^3r(T)$ and ${}^1r(T)$ by the smoothed value

$$ {}^5r(T) \simeq {}^3r(T) \simeq {}^1r(T) \simeq \frac{r(T)}{12}, \qquad (331,8)$$

where $r(T)$ is defined by

$$ r(T) = \sum_{j=0}^{\infty} (2j+1)^2\, e^{-j(j+1)\Theta_r/T}, \qquad (331,9)$$

and so is the complete rotational partition function for an isotropic rotator when symmetry requirements are ignored. When the approximation (8) is valid the three forms of methane will have the same heat capacity and need no longer be distinguished. The complete rotational-nuclear partition function for all forms of methane then becomes

$$ {}^5r_n(T) + {}^3r_n(T) + {}^1r_n(T) = \tfrac{5}{12}r(T) + \tfrac{9}{12}r(T) + \tfrac{9}{12}r(T) = \tfrac{16}{12}r(T). \quad (331,10)$$

The factor 16 in the numerator is the product of the four spin factors 2 of the four H nuclei and the factor 12 in the denominator is the usual symmetry number. From (10) we observe that at high temperatures the three kinds of methane will be in equilibrium in the proportions 5 : 9 : 2. When methane is cooled under normal conditions in the absence of a catalyst these proportions will presumably remain unaltered in the metastable mixture.

The rotational heat capacities of the three forms of methane, of the equi-

* See E. B. Wilson, *J. Chem. Phys.* 3, 276 (1935).

librium mixture and of the metastable mixture have been calculated by MacDougall.* The results of these calculations are shown in Fig. 10. We notice that all the heat capacities are effectively classical at temperatures above 80° K.

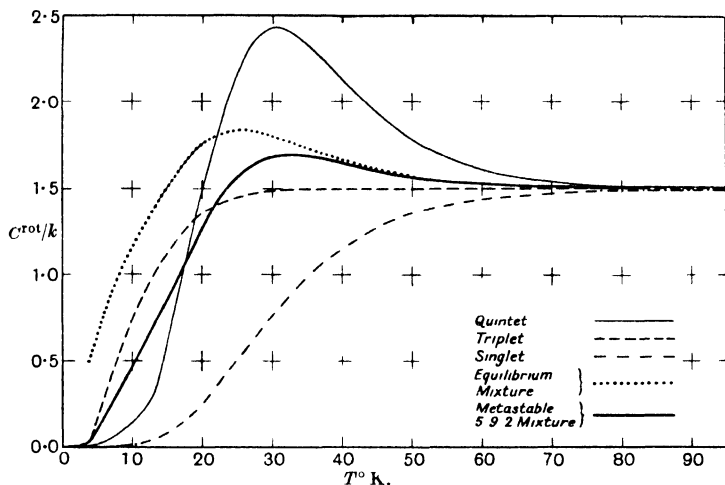



Fig. 10. Rotational heat capacity of $CH_4$.

**§ 332. Equipartition of energy.** The most important classical distribution law which we have not yet included is the theorem of equipartition. This is often stated as follows—*if we have any set of N classical systems in an assembly, each of s degrees of freedom, whose energy (in Hamiltonian form) consists of the sum of $s+t$ square terms ($0 \leqslant t \leqslant s$), then in equilibrium the mean energy of the set is $N(s+t)\,\frac{1}{2}kT$ or $\frac{1}{2}kT$ for each square term in the energy.* The present method enables us to give a simple proof of this theorem, and to indicate its full range of validity, including for example the rotations of a rigid body, which some current proofs do not.

Let us consider an assembly containing $N$ systems $A$, such that the energy $\epsilon$ of each state separates into two terms

$$\epsilon = \epsilon^{\mathrm{cl}} + \epsilon^{\mathrm{qu}}, \qquad (332, 1)$$

the first term $\epsilon^{\mathrm{cl}}$ being the energy corresponding to a number of classical degrees of freedom, and the second term $\epsilon^{\mathrm{qu}}$ corresponding to the remaining degrees of freedom. Then the partition function $f(T)$ for these systems factorizes into $f^{\mathrm{cl}}(T)$ for the classical degrees of freedom and $f^{\mathrm{qu}}(T)$ for the

* MacDougall, *Phys. Rev.* **38**, 2296 (1931). Earlier calculations by Villars and Schultze, *Phys. Rev.* **38**, 998 (1931) are erroneous.

remaining degrees of freedom. The average energy $\overline{E_A}$ of the $N$ systems $A$ will correspondingly split into two terms,

$$\overline{E_A} = \overline{E_A^{\mathrm{cl}}} + \overline{E_A^{\mathrm{qu}}}, \qquad (332, 2)$$

the former being the average energy in the classical degrees of freedom and the latter being the average energy in the remaining degrees of freedom. The theorem of equipartition, which we shall derive, will apply to $\overline{E_A^{\mathrm{cl}}}$, and is independent of the form of $\epsilon^{\mathrm{qu}}$ and the resulting value of $\overline{E_A^{\mathrm{qu}}}$, provided, of course, that the two sets of degrees of freedom are indeed separable as postulated in (1).

Let the number of classical degrees of freedom be $s$, and let us suppose that the potential energy of these classical degrees of freedom is a sum of $t$ square terms in the coordinates $q_1, q_2, \ldots, q_t$, the coefficients being either constants or functions of the remaining $(s-t)$ coordinates $q^*_{t+1}, q^*_{t+2}, \ldots, q^*_s$. We have attached asterisks to the symbols for these coordinates for convenience, so that we may distinguish the two types of coordinates as $q$ and $q^*$. The kinetic energy can always be expressed as a sum of square terms in the conjugate momenta $p_1, p_2, \ldots, p_t, p^*_{t+1}, p^*_{t+2}, \ldots, p^*_s$, and we assume that the coefficients are either constants or functions only of the $q^*_{t+1}, q^*_{t+2}, \ldots, q^*_s$, but not of the $q_1, q_2, \ldots, q_t$. Then the total energy $\epsilon^{\mathrm{cl}}$ of the classical degrees of freedom will be of the form

$$\epsilon^{\mathrm{cl}} = \tfrac{1}{2}\alpha_1 q_1^2 + \tfrac{1}{2}\alpha_2 q_2^2 + \ldots + \tfrac{1}{2}\alpha_t q_t^2 + \tfrac{1}{2}\beta_1 p_1^2 + \tfrac{1}{2}\beta_2 p_2^2 + \ldots + \tfrac{1}{2}\beta_t p_t^2$$
$$+ \tfrac{1}{2}\beta_{t+1} p^{*2}_{t+1} + \tfrac{1}{2}\beta_{t+2} p^{*2}_{t+2} + \ldots + \tfrac{1}{2}\beta_s p^{*2}_s, \qquad (332, 3)$$

where $\alpha_1, \alpha_2, \ldots, \alpha_t$, $\beta_1, \beta_2, \ldots, \beta_s$ are all either constants or functions of $q^*_{t+1}, q^*_{t+2}, \ldots, q^*_s$ only.

Now as the degrees of freedom considered are all classical, the partition function $f^{\mathrm{cl}}(T)$ is equivalent to the classical phase integral, that is to say

$$f^{\mathrm{cl}}(T) = h^{-s} \int \ldots \int dq_1 \ldots dq^*_s \, dp_1 \ldots dp^*_s \, e^{-\epsilon^{\mathrm{cl}}/kT}, \qquad (332, 4)$$

where $\epsilon^{\mathrm{cl}}$ is given by (3). The limits of integration of the coordinates $q$ and the momenta $p$, $p^*$ are all $-\infty$ to $+\infty$, but those of the $q^*$ will be determined by the geometry of the system. Local boundary fields such as those defining the walls of a containing vessel may be regarded alternatively, as shown in § 302, as geometrical variables defining the limits of integration of the $q^*$. Owing to the form of $\epsilon^{\mathrm{cl}}$ given by (3) we can perform the $s+t$ integrations in (4) over the $q$, $p$, $p^*$ and obtain

$$f^{\mathrm{cl}}(T) = h^{-s}(2\pi kT)^{\frac{1}{2}(s+t)} \int \ldots \int dq^*_{t+1} \ldots dq^*_s (\alpha_1 \ldots \alpha_t \beta_1 \ldots \beta_s)^{-\frac{1}{2}}, \qquad (332, 5)$$

the integral being now a pure function of the $q^*$ only. For the average energy

in the classical degrees of freedom of the $N_A$ system we have

$$\overline{E_A^{\text{cl}}} = NkT^2 \frac{\partial \log f^{\text{cl}}(T)}{\partial T} = N(s+t)\,\tfrac{1}{2}kT. \qquad (332,6)$$

Thus the average energy of the classical degrees of freedom per system is one unit of $\frac{1}{2}kT$ for each square term of (3). This is an accurate statement of the theorem of equipartition of energy.

A slightly more general form of this theorem has been derived,* but the form given above is sufficiently general for all important applications. In particular we may mention the following. The average translational kinetic energy per molecule (in three dimensions) is $\frac{3}{2}kT$. The average (kinetic) energy of a classical rotator without axial spin is $kT$. The average (kinetic) energy of a classical top (symmetrical or unsymmetrical) is $\frac{3}{2}kT$. The simple harmonic oscillator has two square terms in its Hamiltonian energy and its classical energy content is therefore $kT$, in agreement with (320, 9) when $h\nu/kT \to 0$.

**§ 333. Equipartition of kinetic energy.** Let us again consider an assembly containing $N$ systems $A$ whose energy $\epsilon$ separates, according to (332, 1), into $\epsilon^{\text{cl}}$, the energy corresponding to a number $s$ of classical degrees of freedom and $\epsilon^{\text{qu}}$, the energy of the other degrees of freedom. Suppose now that $\epsilon^{\text{cl}}$ has the somewhat more general form

$$\epsilon^{\text{cl}} = \epsilon^{\text{pot}}(q_1, \ldots, q_s) + \tfrac{1}{2}\beta_1 p_1^2 + \ldots + \tfrac{1}{2}\beta_s p_s^2, \qquad (333,1)$$

where the potential energy $\epsilon^{\text{pot}}$ is a function of $q_1, \ldots, q_s$, and $\beta_1, \ldots, \beta_s$ may now be functions of $q_1, \ldots, q_s$. On classical theory we may discuss separately the distribution of kinetic and of potential energy. The kinetic energy $\epsilon^{\text{kin}}$ is given by

$$\epsilon^{\text{kin}} = \tfrac{1}{2}\beta_1 p_1^2 + \ldots + \tfrac{1}{2}\beta_s p_s^2. \qquad (333,2)$$

Then on classical theory the average number of systems in a state corresponding to the element of phase space $dq_1 \ldots dq_s\, dp_1 \ldots dp_s$ will be

$$N \frac{dq_1 \ldots dq_s\, dp_1 \ldots dp_s\, e^{-(\epsilon^{\text{pot}}+\epsilon^{\text{kin}})/kT}}{\int \cdots \int dq_1 \ldots dq_s\, dp_1 \ldots dp_s\, e^{-(\epsilon^{\text{pot}}+\epsilon^{\text{kin}})/kT}}. \qquad (333,3)$$

Consequently the average value of the kinetic energy will be

$$N \frac{\int \cdots \int dq_1 \ldots dq_s\, dp_1 \ldots dp_s\, \epsilon^{\text{kin}}\, e^{-(\epsilon^{\text{pot}}+\epsilon^{\text{kin}})/kT}}{\int \cdots \int dq_1 \ldots dq_s\, dp_1 \ldots dp_s\, e^{-(\epsilon^{\text{pot}}+\epsilon^{\text{kin}})/kT}}. \qquad (333,4)$$

If we substitute the value of $\epsilon^{\text{kin}}$ from (2), we can perform the integrations

* See *S.M.* p. 61.

over $p_1, \ldots, p_s$, and obtain simply $\frac{1}{2}NskT$, the remaining integrals in $q_1, \ldots, q_s$ cancelling.

We have thus obtained the important result that in classical theory the average kinetic energy of each system is one unit $\frac{1}{2}kT$ for each classical degree of freedom. This theorem enables us to conclude that the average kinetic energy, on classical theory, of a linear anharmonic oscillator will be $\frac{1}{2}kT$ and of a three-dimensional anharmonic oscillator $\frac{3}{2}kT$. The potential energy for these systems is, however, not given by the equipartition formula.

**§ 334. Averages for molecules crossing a plane.** The average properties which we have hitherto deduced have been averages for all the molecules in a bounded volume at a given instant of time. They are not the same as the averages for all the molecules crossing a plane in a bounded time interval, because relatively more fast molecules cross the plane than slow ones in the same time interval. We shall now derive some of these averages for the molecules crossing a plane, as these have important applications, particularly in connection with rates of condensations at a liquid or solid surface.

It can be verified that the distribution of velocities and the average kinetic energy in directions parallel to the plane are the same for all molecules crossing the plane in a bounded time as for all the molecules in a bounded volume at a given instant. We need therefore consider only the distribution of velocities and the average kinetic energy in the direction normal to the plane, taken as the axis $x$. Then the number of molecules with a given velocity component $u$ in the $x$-direction which cross an area $A$ of the plane in a time interval $\tau$ is equal to the number of molecules with the given velocity component, which at any instant are contained in a box of cross-section $A$ and length $u\tau$. This number is by (303, 5)

$$\frac{N}{V} Au\tau \left(\frac{m}{2\pi kT}\right)^{\frac{1}{2}} e^{-\frac{1}{2}mu^2/kT}\, du. \qquad (334, 1)$$

The total number of molecules of unprescribed velocity crossing an area of the surface, say from left to right, is obtained by integrating (1) from $u = 0$ to $u = \infty$. We obtain

$$\frac{N}{V} A\tau \left(\frac{m}{2\pi kT}\right)^{\frac{1}{2}} \int_0^\infty e^{-\frac{1}{2}mu^2/kT} u\, du = \frac{N}{V} A\tau \left(\frac{kT}{2\pi m}\right)^{\frac{1}{2}} = pA\tau(2\pi mkT)^{-\frac{1}{2}}, \qquad (334, 2)$$

where $p$ denotes the partial vapour pressure.

We shall now calculate the average kinetic energy in the $x$-direction of all the molecules crossing area $A$ of a plane normal to the $x$-direction in the time interval $\tau$. The number of such molecules with velocity component in

the $x$-direction between $u$ and $u+du$ is given by (1), and these molecules have kinetic energy $\frac{1}{2}mu^2$ in the $x$-direction. The average value of the $x$-kinetic energy for all molecules crossing the surface is therefore

$$\frac{\int_0^\infty \frac{1}{2}mu^2 \frac{N}{V} Au\tau\left(\frac{m}{2\pi kT}\right)^{\frac{1}{2}} e^{-\frac{1}{2}mu^2/kT}\,du}{\int_0^\infty \frac{N}{V} Au\tau\left(\frac{m}{2\pi kT}\right)^{\frac{1}{2}} e^{-\frac{1}{2}mu^2/kT}\,du} = \frac{\int_0^\infty \frac{1}{2}mu^3\, e^{-\frac{1}{2}mu^2/kT}\,du}{\int_0^\infty ue^{-\frac{1}{2}mu^2/kT}\,du} = kT. \tag{334, 3}$$

We see from (3) that, for the molecules crossing a surface in a given time interval, the average kinetic energy in the $x$-direction normal to the surface is just double the average value in the $y$- or $z$-directions which are parallel to the surface. In Chapter XII we shall derive formulae for pairs of colliding molecules, and there again we shall find that the average relative kinetic energy in the direction of the line of centres is $kT$, as compared to $\frac{1}{2}kT$ for each of the two directions at right angles to the line of centres.

**§ 335. Small corrections to the perfect gas laws due to non-classical statistics.** As is clear from the discussion in § 219 a deviation from classical statistics ($\lambda \ll 1$) might be barely appreciable for $H_2$ and perhaps He at very low temperatures. Both these molecules contain an even number of electrons, an even number of protons and an even number of neutrons. The assembly eigen functions will therefore be symmetrical with respect to the molecules when these are taken as the independent systems forming the assembly. The assembly of molecules will therefore obey the Bose-Einstein statistics.

It is, however, uncertain whether any deviation due to the difference between Bose-Einstein statistics and classical statistics could be disentangled from the corrections to the perfect gas laws due to intermolecular forces. We shall therefore not give detailed formulae.

Footnote to p. 118. Kistiakowsky, Lacher and Stitt, *J. Chem. Phys.* **7**, 289 (1939), report new measurements of the heat capacity of $C_2H_6$ in the range 92° K. to 134° K., and of $C_2D_6$ in the range 93° K. to 334° K. These measurements establish beyond reasonable doubt that the potential energy associated with the twisting mode can, at least for small values of $\phi$, be represented by formula (328, 3), with $u^0/k = 1380$ deg.

## CHAPTER IV

### CRYSTALS

**§ 400. Introduction.** In order to apply statistical mechanics to a crystal, we regard the whole crystal as a single Hamiltonian system, whose classical motion may, to a first approximation, be regarded as small oscillations about a position of equilibrium, and can be analysed into its normal modes. Each of these, to this first approximation, is an independent simple harmonic oscillation. This analysis will adequately represent the motion so long as the general run of the oscillations is small enough, that is so long as the crystal is not too hot. At greater violence of oscillation terms in the potential energy of higher order than the squares of the displacements must be introduced, but we shall not investigate these effects here. To transcribe this classical theory into quantal theory we have merely to assign the quantum states of the harmonic oscillator to each of the normal modes.

The construction of the partition function to this approximation demands only an enumeration of the frequencies of the normal modes of the crystal consisting of a given number of molecules, and is precisely as accurate as the enumeration. It is difficult, however, to make an accurate enumeration, and various approximate enumerations have been given, more or less based on guesswork. The earliest was Einstein's* who suggested that, for a crystal containing $N$ atoms, it was sufficiently accurate to take all the $3N$ frequencies equal. This still remains a valuable rough approximation. It was improved by Debye† who suggested that the $3N$ frequencies could be taken to be the $3N$ lowest frequencies of a *continuum* with the same elastic constants as the actual atomic crystal. This suggestion has proved of great importance, and we shall give an account of Debye's theory in the somewhat more general form into which it was cast by Born.‡ The theory is very successful in accounting for observed facts, so successful that it has been strained beyond its natural range, and facts which do not fit it have been thought to be anomalous and to require special explanations without due cause. It has only recently been realized, thanks to the work of Blackman,§ that Debye's suggestion for the frequencies of the normal modes, even as elaborated by Born, may be a much less good approximation than it was

* Einstein, *Ann. d. Phys.* **22**, 180, 800 (1907); **34**, 170, 590 (1911).

† Debye, *Ann. d. Phys.* **39**, 789 (1912).

‡ Born, "Atomtheorie des festen Zustandes", *Encycl. Math. Wiss.* **5**, part 3, no. 25 (1923); Born and Göppert-Mayer, "Dynamische Gittertheorie der Kristalle", *Handb. d. Physik*, Ed. 2, **24**, part 2, 623 (1933).

§ Blackman, *Proc. Roy. Soc.* A, **148**, 365, 384 (1935); **149**, 117, 126 (1935); **159**, 416 (1937).

formerly held to be. Considerable caution is therefore required before departures from Debye's theory can be held to indicate anything more than slight errors in the assumed distribution of the frequencies of the normal modes.

It is possible here to give only an elementary study of the equilibrium properties of perfect crystals; in particular no attempt is made to deduce these properties from assumed lattice structures and laws of force.* The study of crystal imperfections is taken up in Chapter XIII. As a first step we consider the normal modes and partition function of an elastic continuum.

**§ 401. The normal modes of a continuous elastic solid.** In order to construct a partition function for a continuous elastic solid, we must analyse the degrees of freedom according to their natural frequencies. We assume that any steady internal motion of the medium may be described by a superposition of stationary harmonic waves, each such wave being characterized by a direction of vibration, a frequency, and an amplitude. For a wave in a given direction in an elastic solid there are three independent directions of vibration, one longitudinal and two transverse. If we know the frequency of a possible wave, we can use the partition function for a harmonic oscillator of this frequency to calculate the average value for its energy, which is equivalent to calculating the average value of the amplitude. Thus the whole problem resolves itself into a determination of the possible values of the frequency. Now the determination of the possible values of the wave length is easy. Let us suppose the medium contained in a rectangular box defined by

$$0 \leqslant x \leqslant a, \quad 0 \leqslant y \leqslant b, \quad 0 \leqslant z \leqslant c. \tag{401, 1}$$

Then for a wave travelling parallel to the $x$-axis the half wave length $\frac{1}{2}\lambda$ must be an integral sub-multiple of the length $a$ of the box; that is to say

$$2/\lambda = l/a \quad (l \text{ integral}). \tag{401, 2}$$

Similar conditions hold for waves parallel to the $y$- and $z$-axes. For a wave travelling in any direction, it can be shown that the boundary conditions of the box lead to the general restriction on the wave length

$$\left(\frac{2}{\lambda}\right)^2 = \left(\frac{l}{a}\right)^2 + \left(\frac{m}{b}\right)^2 + \left(\frac{n}{c}\right)^2 \quad (l,\, m,\, n \text{ integral}). \tag{401, 3}$$

Hence for a given type of vibration, say longitudinal, the number of possible wave lengths greater than $\lambda_0$ is equal to the number of positive integers $l, m, n$ satisfying

$$\left(\frac{l}{a}\right)^2 + \left(\frac{m}{b}\right)^2 + \left(\frac{n}{c}\right)^2 \leqslant \left(\frac{2}{\lambda_0}\right)^2. \tag{401, 4}$$

* The reader may refer to *S.M.*, Chapter X, for some account of this field.

This is equal to the number of points $\xi$, $\eta$, $\zeta$ with positive integral coordinates inside the ellipsoid

$$\left(\frac{\xi}{a}\right)^2+\left(\frac{\eta}{b}\right)^2+\left(\frac{\zeta}{c}\right)^2=\left(\frac{2}{\lambda_0}\right)^2, \tag{401, 5}$$

and therefore to the volume of an octant of this ellipsoid, namely

$$\frac{1}{8}\frac{4\pi}{3}\frac{abc}{(\frac{1}{2}\lambda_0)^3}=\frac{4\pi}{3}\frac{V}{\lambda_0^3}, \tag{401, 6}$$

where $V$ is the volume of the box. It can moreover be shown that this dependence on $V$ is independent of the shape of the box as soon as the wave length becomes small compared with the dimensions of the box, and it is only such modes which are numerous enough to matter. Now the velocity of longitudinal waves in a continuous medium is the same for all wave lengths, and, if the medium is isotropic, the same for all directions; calling this value of the velocity $c_l$, the frequency $\nu$ is related to the wave length $\lambda$ by

$$\lambda\nu = c_l. \tag{401, 7}$$

Hence the number of possible frequencies less than $\nu_0$ for longitudinal waves is

$$\frac{4\pi}{3}\frac{\nu_0^3}{c_l^3}V. \tag{401, 8}$$

Similarly, if the velocity of all transverse waves is $c_t$, then, remembering that there are two independent transverse directions of vibration, the total number of frequencies less than $\nu_0$ for transverse waves is

$$2\frac{4\pi}{3}\frac{\nu_0^3}{c_t^3}V \tag{401, 9}$$

The total number of independent waves, longitudinal or transverse, with frequencies less than $\nu_0$ is then

$$\frac{4\pi}{3}V\left(\frac{1}{c_l^3}+\frac{2}{c_t^3}\right)\nu_0^3. \tag{401, 10}$$

Finally, the number of independent waves with frequencies between $\nu$ and $\nu+d\nu$, by differentiation of (10), is

$$4\pi V\left(\frac{1}{c_l^3}+\frac{2}{c_t^3}\right)\nu^2 d\nu. \tag{401, 11}$$

This classical analysis into normal modes is easily translated into quantum theory. To the approximation used in this classical analysis, Schrödinger's equation for the medium can be so transformed that it separates into a set of equations for simple harmonic oscillators, one for each normal mode, with the same frequencies $\nu$ distributed according to (11). It is therefore easy to construct the partition function to this approximation.

§ 402. **The partition function for a continuous medium.** It is convenient to define an average velocity $c$ for waves, longitudinal or transverse, by the equation

$$\frac{3}{c^3} = \frac{1}{c_l^3} + \frac{2}{c_t^3}. \tag{402, 1}$$

The number of normal modes with frequencies between $\nu$ and $\nu + d\nu$ then becomes

$$\frac{12\pi V}{c^3} \nu^2 d\nu. \tag{402, 2}$$

Now each of these modes, regarded as a harmonic oscillator, whose energy zero is assumed to be its lowest quantum state, has according to (320, 2) the partition function

$$(1 - e^{-h\nu/kT})^{-1}. \tag{402, 3}$$

Consequently the partition function $f(T)$ for the whole medium is given by the continued product of factors such as (3), each raised to the power given by (2). Taking logarithms we obtain

$$\log f(T) = -\frac{12\pi V}{c^3} \int_0^\infty \nu^2 \log(1 - e^{-h\nu/kT})\, d\nu. \tag{402, 4}$$

§ 403. **Temperature radiation.** As an example of a truly continuous medium, we shall digress for a moment to consider the temperature radiation in an enclosure containing no matter. Except for one modification we may apply the formulae of the preceding section directly. As the electromagnetic vibrations of radiation in empty space are only transverse and not longitudinal, we have only the second term in (401, 11). The partition function (402, 4) must therefore be multiplied by the factor 2/3 and we obtain for the partition function $R(T)$ of temperature radiation

$$\begin{aligned} \log R(T) &= -\frac{8\pi V}{c^3} \int_0^\infty \nu^2 \log(1 - e^{-h\nu/kT})\, d\nu \\ &= -\frac{8\pi V k^3 T^3}{c^3 h^3} \int_0^\infty \xi^2 \log(1 - e^{-\xi})\, d\xi, \end{aligned} \tag{403, 1}$$

where $c$ is the velocity of light. Using the power series for the logarithm, and then integrating term by term, we have

$$\begin{aligned} -\int_0^\infty \xi^2 \log(1 - e^{-\xi})\, d\xi &= \int_0^\infty \sum_{n=1}^\infty \frac{\xi^2}{n} e^{-n\xi}\, d\xi \\ &= \sum_{n=1}^\infty \frac{1}{n^4} \int_0^\infty \eta^2 e^{-\eta}\, d\eta = 2 \sum_{n=1}^\infty \frac{1}{n^4} = \frac{\pi^4}{45}. \end{aligned} \tag{403, 2}$$

Substituting (2) into (1) we obtain

$$\log R(T) = \frac{8\pi^5 k^3}{45 c^3 h^3} T^3 V. \tag{403, 3}$$

The equilibrium energy of the radiation is given by

$$E^{\text{rad}} = kT^2 \frac{\partial}{\partial T} \log R(T) = \frac{8\pi^5 k^4}{15c^3 h^3} T^4 V, \qquad (403, 4)$$

which is the Stefan-Boltzmann law of total radiation with the theoretical value $8\pi^5k^4/15c^3h^3$ for Stefan's constant.

To obtain the energy in any particular frequency range we factorize $R(T)$ into a factor $R_1(T)$ for the range $\nu$, $\nu+d\nu$, and $R_2(T)$ for the remaining frequencies. Then according to (1) we have

$$\log R_1(T) = -\frac{8\pi V}{c^3} \nu^2 \log(1-e^{-h\nu/kT})\, d\nu. \qquad (403, 5)$$

It follows that $E_\nu d\nu$, the energy in this frequency range, is given by

$$E_\nu d\nu = kT^2 \frac{\partial}{\partial T} \log R_1(T) = \frac{8\pi h}{c^3} V \frac{\nu^3 d\nu}{e^{h\nu/kT}-1}. \qquad (403, 6)$$

This is Planck's law for the energy distribution, from which the quantum theory originated. When we have discussed the thermodynamic functions of a crystal in § 408, it will become clear that the free energy $F^{\text{rad}}$ of radiation is given by

$$F^{\text{rad}} = -kT \log R(T) = -\frac{8\pi^5 k^4}{45c^3 h^3} T^4 V. \qquad (403, 7)$$

The pressure $P^{\text{rad}}$ of radiation is therefore

$$P^{\text{rad}} = -\frac{\partial F^{\text{rad}}}{\partial V} = \frac{8\pi^5 k^4}{45c^3 h^3} T^4, \qquad (403, 8)$$

in agreement with the electrodynamic relationship

$$P^{\text{rad}} = \tfrac{1}{3} E^{\text{rad}}/V. \qquad (403, 9)$$

§ 404. **Crystals of structureless atoms.** We now return to the proper theme of this chapter. For simplicity we begin with a crystal composed of $N$ structureless atoms. We shall extend the treatment later to crystals containing several kinds of atoms with internal structure.

A continuous medium has an infinity of normal modes. An actual crystal such as we consider here can have only a finite number, $3N$, corresponding to its $3N$ degrees of freedom. We do not know exactly how the frequencies of these modes are distributed. Let us suppose that there are $Ng(\nu)\,d\nu$ modes, with frequencies in the range $\nu$, $\nu+d\nu$. Then in place of (402, 4), which would hold only for a continuum, we have at once for the partition function $K(T)$ of the crystal

$$\log K(T) = -N\int_0^\infty g(\nu) \log(1-e^{-h\nu/kT})\, d\nu. \qquad (404, 1)$$

Since there are $3N$ modes in all

$$\int_0^\infty g(\nu)\,d\nu = 3. \qquad (404,2)$$

The distribution function $g(\nu)$ has recently been elaborately reinvestigated by Blackman. By carrying further the older work of Born,* he has shown that it is possible to make certain general statements about $g(\nu)$, but in no case does it appear to be possible to give it any simple analytic form. The following statements are, however, true.

(i) There is a maximum frequency $\nu_{\text{max}}$ such that $g(\nu) = 0$ for $\nu > \nu_{\text{max}}$; the upper limit of integration in (1) and (2) may therefore be replaced by $\nu_{\text{max}}$.

(ii) For small frequencies and consequently long wave lengths, the frequency distribution for the modes of a crystal is the same as that for a continuum with the same elastic constants, so that

$$g(\nu) \sim \alpha\nu^2 \quad (\nu \to 0,\ \alpha \text{ constant}). \qquad (404,3)$$

(iii) As $\nu$ increases from very small values it is usually, though perhaps not universally, true that $g(\nu)$ at first increases faster than $\alpha\nu^2$, taking the form

$$g(\nu) \sim \alpha\nu^2 + \beta\nu^4 \quad (\beta > 0). \qquad (404,4)$$

(iv) During the later stages $g(\nu)$ may show two or more distinct peaks. In certain cases which have been studied in detail, one of these maxima is close to $\nu_{\text{max}}$, where $g(\nu)$ descends very steeply to its final zero value.

This behaviour of $g(\nu)$ is illustrated in Fig. 1, constructed† for a simple cubic lattice with the arbitrary ratio 20 : 1 of the force constant for nearest neighbours to the force constant for next nearest neighbours, interactions between atoms farther apart being neglected.[A]

Owing to the complicated form of $g(\nu)$ the resulting properties of the partition function cannot be simply formulated, and it is still necessary to use partition functions derived from simplified forms of $g(\nu)$, which were first proposed when the true form was quite unknown. As we have already mentioned in § 400, the inherent inaccuracies in these $g(\nu)$'s must always be remembered when the resulting formulae are compared with experiment.

Einstein's approximation consists in putting $g(\nu) = 0$ except for an infinitesimal range of values near $\nu_E$, say, where all the values are supposed to congregate, so that (2) is still true. Such an assumption leads therefore to

$$\log K(T) = -3N \log(1 - e^{-h\nu_E/kT}). \qquad (404,5)$$

This is at first sight very crude, but actually $g(\nu)$ usually has a very pro-

* Born and Von Kármán, *Physikal. Zeit.* **13**, 297 (1912).

† Blackman, *Proc. Roy. Soc.* A, **159**, 416 (1937).

[A] See appendix, § A 1.

nounced peak near $\nu_{max}$, so that for high and moderate temperatures, where $kT > h\nu_{max}$ or $kT \simeq h\nu_{max}$, Einstein's approximation represents the most important part of $g(\nu)$ with reasonable accuracy, and may still be used with

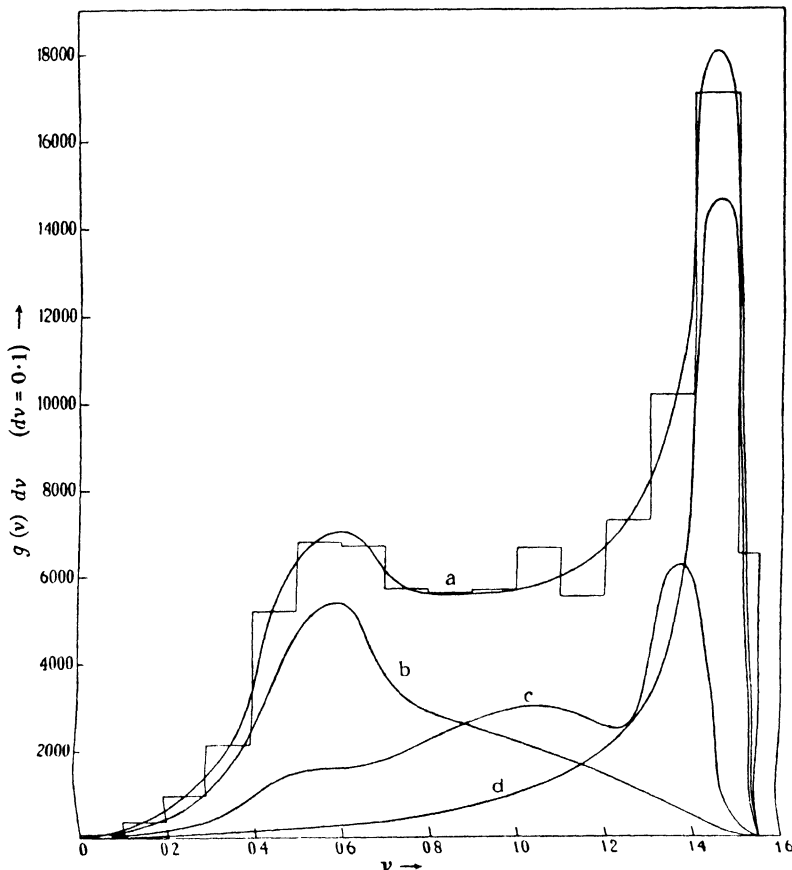



Fig. 1. The density of normal vibrations as a function of the frequency for a simple cubic lattice for a ratio 0·05 of the force constant between next closest neighbours to the force constant between closest neighbours ($\nu_D = 1{\cdot}32$, $\nu_{max} = 1{\cdot}55$ in arbitrary units; the unit of the density is such that the total number of points is 89,373). The upper curve *a* represents the total spectrum, the lower curves *b*, *c*, *d* the spectrum for each of three frequency branches. The "step" curve through which curve *a* is drawn is given to illustrate the method used in constructing the curves. The "steps" are obtained by calculation and represent the total number of vibrations (i.e. total area) for a frequency range of 0·1; the curves are drawn through these "steps" in such a way as to keep the area under the curve equal to the area of the "step" for any particular frequency range.

advantage in rough investigations on account of its simplicity. It is, however, necessarily very inaccurate at low temperatures, where the low

frequency modes for which $h\nu \simeq kT$ will give the dominant contributions to the true partition function.

Debye's approximation preserves the correct low frequency form (3) of $g(\nu)$, but assumes that this form holds for all frequencies until a frequency $\nu_D$ is reached, such that the right number of modes has been included; that is, $\nu_D$ is chosen so that

$$3 = \int_0^{\nu_D} \alpha\nu^2 d\nu = \tfrac{1}{3}\alpha\nu_D^3. \qquad (404, 6)$$

The complete specification of Debye's $g(\nu)$ is therefore

$$\left.\begin{aligned} g(\nu) &= 9\nu^2/\nu_D^3 \quad (\nu \leqslant \nu_D), \\ g(\nu) &= 0 \qquad\quad (\nu > \nu_D). \end{aligned}\right\} \qquad (404, 7)$$

One constant $\nu_D$ (or $\alpha$) remains to be specified in Debye's theory. This is actually done, as we shall see, in a variety of ways. From the present point of view the correct method is to determine $\alpha$ so that the long waves are distributed like those of a continuum with the same elastic constants, which implies that $\alpha$ and so $\nu_D$ can be calculated in terms of the observed elastic constants of the material. On Debye's assumption the partition function is given by

$$\log K(T) = -\frac{9N}{\nu_D^3}\int_0^{\nu_D} \nu^2 \log(1-e^{-h\nu/kT})\,d\nu. \qquad (404, 8)$$

On referring to (402, 4) we see that $\log K(T)$ can also be put in the form

$$\log K(T) = -\frac{12\pi V}{c^3}\int_0^{\nu_D} \nu^2 \log(1-e^{-h\nu/kT})\,d\nu; \qquad (404, 9)$$

thus, if Debye's distribution of frequency is adjusted to fit the actual distribution for low frequencies,

$$\nu_D^3 = \frac{N}{V}\frac{3c^3}{4\pi}, \qquad (404, 10)$$

where $c$ is the mean velocity of sound for long waves in the crystal defined by (402, 1), and calculable from the elastic constants.

It is convenient to define a temperature $\Theta_D$ by the relation

$$\Theta_D = \frac{h\nu_D}{k} = \frac{hc}{k}\left(\frac{3N}{4\pi V}\right)^{\frac{1}{3}}. \qquad (404, 11)$$

In terms of $\Theta_D$ we can rewrite (8) as

$$\log K(T) = -9N\frac{T^3}{\Theta_D^3}\int_0^{\Theta_D/T} \xi^2 \log(1-e^{-\xi})\,d\xi. \qquad (404, 12)$$

If we integrate this by parts, we obtain the alternative form

$$\log K(T) = -3N\log(1-e^{-\Theta_D/T}) + 3N\frac{T^3}{\Theta_D^3}\int_0^{\Theta_D/T} \frac{\xi^3}{e^{\xi}-1}\,d\xi. \qquad (404, 13)$$

The first term has the form of Einstein's approximation, while the second term becomes relatively unimportant when $T \gg \Theta_D$. Hence we see that when $T \gg \Theta_D$ Einstein's approximation is practically as good as Debye's.

We shall discuss the application of Debye's approximations in some detail to actual crystals. After doing so we shall return to consider what modifications would be introduced into the theory by the use of a more accurate $g(\nu)$.

**§ 405. Contribution of electrons and nuclei to partition functions.** In the preceding section we have derived the form of the partition function for a crystal formed of structureless systems all alike. We must now consider briefly what modification, if any, must be introduced to take account of the electronic structure of actual atoms. We shall still use a crude approximation. The conclusions reached are sufficiently accurate for almost all applications, and are on the whole confirmed by a deeper analysis of the electronic behaviour. We assume that the electrons are either very tightly bound to nuclei or only loosely bound. The tightly bound electrons may then be treated as attached each to a specific nucleus forming an atomic core. *The atomic cores are effectively localized systems, and therefore each introduces a factor $e(T)$, or $[e(T)]^N$ in all, into the complete partition function*, where $e(T)$ is the partition function for the electronic states of the core. Usually only the lowest electronic energy level will contribute appreciably to $e(T)$, and $e(T)$ then reduces to its first term. If then as usual we take the zero of electronic energy as that of the normal electronic state, $e(T)$ reduces to $\varpi_0$, the statistical weight of the lowest electronic energy level. The remaining electrons, if any, usually referred to as free electrons, may be thought of as moving freely in a periodic potential field. For our present purpose it is sufficiently accurate to average out this periodic field, and treat the electrons as moving in a uniform potential. They will then obey the statistical laws of an assembly of particles in a uniform enclosure. These laws will not, however, be the familiar laws of perfect gases on account of the small mass and high concentration of the electrons, which cause condition (219, 14) to fail. In fact at all temperatures up to about 2000° K. we have the opposite state of affairs, $\lambda \gg 1$. In simple physical terms this means that instead of the number of states of low energy being much more numerous than the number of electrons, there is on the contrary a scarcity of low energy states. Consequently the electrons all crowd into the lowest energy states available. The state of the assembly of electrons is completely determined by the condition that all the lowest translational states are occupied, each by two* electrons, and all the remainder are empty. In other words there

* Two, because to each translational state there correspond two states of electron spin.

is only one state of the collection of free electrons that contributes appreciably to the average properties of the assembly. Consequently we are led to the strikingly simple result that the contribution to the partition function of the crystal from all the free electrons is just the factor unity. This conclusion will be confirmed by more precise reasoning in Chapter XI. The present discussion has been purposely simplified; the electrons may sometimes even make important contributions to the heat capacity.

Finally we have to introduce an orientational weight factor $\rho$ for the nuclear spin.

Introducing the new factor $v_0$ for the bound electrons, the factor unity for the free electrons, and the factor $\rho$ for the nuclear spins, we obtain for the complete partition function of an atomic crystal, in place of (404, 1),

$$\log K(T) = -N\int_0^\infty g(\nu)\log(1-e^{-h\nu/kT})\,d\nu + N\log v_0\rho. \quad (405, 1)$$

It is to be remembered that this partition function has been constructed by using for energy zero the state of lowest energy of the crystal, which includes the residual energy $\frac{1}{2}h\nu$ in each normal mode. In § 408 we shall revise our energy zero.

**§ 406. The average properties of a crystal.** We have so far analysed the motion of the crystal into that of a set of $3N$ localized simple harmonic oscillators. For many purposes it is unnecessary to be so precise, and we may then merely suppose that the $3N$ localized oscillators are anharmonic, each with a partition function of the more general form

$$f_\tau(T) = \Sigma_r\, e^{-\epsilon_r/kT}, \quad (406, 1)$$

the suffix $\tau$ referring to the $\tau$th oscillator. The partition function $K(T)$ for the crystal is then given by

$$\log K(T) = \sum_1^{3N} \log f_\tau(T) + N\log v_0\rho, \quad (406, 2)$$

if we continue to use the same approximations for the electronic and nuclear contributions.

It has been convenient above to use the natural frequency of the oscillators as a classifying parameter, allowing us to group together a large number $Ng(\nu)\,d\nu$ of oscillators of practically indistinguishable properties, which can then be treated as a typical assembly of identical localized systems. It is by no means essential that the frequency should be chosen for this purpose. In the more general case any parameter $\tau$ might be chosen, provided merely that it enables us to select groups of oscillators, $N_\tau = Ng(\tau)\,d\tau$ in number, all of which have practically the same states and partition functions. Using

any such classification we can rewrite (2) in the form

$$\log K(T) = N\int g(\tau)\log f_\tau(T)\,d\tau + N\log v_0\rho, \qquad (406, 3)$$

and may also at once apply formula (227, 3), and find for the number $\overline{n_r}$ of oscillators of the $\tau$th group in their $r$th state

$$\overline{n_r} = N_\tau \frac{e^{-\epsilon_r/kT}}{f_\tau(T)}. \qquad (406, 4)$$

Whenever our arguments require $N_\tau$ to be large, this may be guaranteed by making $N$ large enough. The other properties of the crystal, such as its energy or external reactions, can always be calculated by the use of $\overline{n_r}$ as given by (4).

Though in fact it is always possible to group the oscillators of an actual system in some such manner into large groups, at least with the same accuracy as an analysis into separate normal modes is itself possible, we shall find in the following section that this grouping is really not essential, and can be omitted without any effect on the results for the energy and reactions. If we start with $\log K(T)$ as given by (2) and apply (4) with $N = 1$ to each distinct oscillator, we always arrive at the same results as we find by prior grouping. With this use of the formula (4), $\overline{n_r}$ is always a fraction less than unity. On referring back to the general proofs of such formulae in Chapter II we see that there is nothing in these proofs which requires any particular $\overline{n_r}$ to be large, unless we want to study the fluctuation of the equilibrium values so determined. If therefore part of one large assembly is a single system, and we calculate formally $\overline{n_r}$ for a particular state or set of states for this system, the value so calculated will be the average or equilibrium value of the fractional "number" of systems found in the specified state. Since by our fundamental assumption averaging over phase space is equivalent to a time average, the fraction calculated for our system is the fraction of time during which it occupies the specified state or states as a member of the given large assembly. This interpretation is quite general, and frequently useful for complicated single systems. We can express it in the general form that if $K(T)$ is the partition function for a system and $\delta K(T)$ that part of it which corresponds to any selected sets of states, the fraction of time that the assembly spends with the system in that set of states is $\delta K(T)/K(T)$.

This statement, which is here a deduction from the fundamental hypothesis we have adopted, may be shown to be precisely equivalent to Gibbs' fundamental hypothesis, in a form adapted to quantal assemblies as well as classical.

§ 407. **Energy and external reactions of crystals.** In setting up the formula for the energy of a crystal, we shall start by supposing large groups of oscillators to have been formed, and apply (406, 4). We shall end by verifying that prior grouping is unnecessary. Having formed the groups, the average energy in the $\tau$th group, referred to the energy zero used in (406, 1), is given by

$$\overline{E_\tau} = \Sigma_r \overline{n_r}\epsilon_r = N_\tau \Sigma_r \epsilon_r e^{-\epsilon_r/kT}/f_\tau(T) = N_\tau kT^2 \frac{\partial}{\partial T}\log f_\tau(T). \quad (407, 1)$$

Taking $N_\tau = Ng(\tau)\,d\tau$ and summing for all $\tau$, we find

$$\overline{E} = \Sigma_\tau \overline{E_\tau} = N\int d\tau\, g(\tau)\, kT^2 \frac{\partial}{\partial T}\log f_\tau(T)$$

$$= NkT^2\frac{\partial}{\partial T}\int g(\tau)\log f_\tau(T)\,d\tau = kT^2\frac{\partial}{\partial T}\log K(T), \quad (407, 2)$$

where $K(T)$ is given by (406, 3).

If we proceed without grouping we use (406, 4) with $N_\tau = 1$ and find

$$\overline{E_\tau} = kT^2\frac{\partial}{\partial T}\log f_\tau(T). \quad (407, 3)$$

Summing now over all oscillators and using (406, 2) for $K(T)$ we find

$$\overline{E} = \Sigma_\tau \overline{E_\tau} = kT^2\frac{\partial}{\partial T}\Sigma_\tau \log f_\tau(T) = kT^2\frac{\partial}{\partial T}\log K(T) \quad (407, 4)$$

as before. In future we shall not trouble to form groups.

If the energy levels $\epsilon_r$ of the mode $\tau$ depend on a parameter $x$, then the average value $\overline{X_\tau}$ of the corresponding generalized force exerted on the outside world by the $\tau$th oscillator is given by

$$\overline{X_\tau} = \Sigma_r \overline{n_r}\left(-\frac{\partial \epsilon_r}{\partial x}\right) = -\Sigma_r \frac{\partial \epsilon_r}{\partial x} e^{-\epsilon_r/kT}/f_\tau(T) = kT\frac{\partial}{\partial x}\log f_\tau(T). \quad (407, 5)$$

It follows that the average value $\overline{X}$ of the generalized force exerted by the crystal is given by

$$\overline{X} = \Sigma_\tau \overline{X_\tau} = kT\,\Sigma_\tau \frac{\partial}{\partial x}\log f_\tau(T) = kT\frac{\partial}{\partial x}\log K(T). \quad (407, 6)$$

This formula for the force exerted by a single crystal is the analogue of (225, 7) for the force exerted by an assembly of free (gaseous) systems.

§ 408. **Thermodynamic functions of a crystal. Revision of energy zero.** Having now obtained statistical formulae for the average (equilibrium) properties of a crystal we can transcribe these into thermodynamic form. This transcription is achieved most simply by defining the function $F$ by the equation

$$F = -kT\log K(T). \quad (408, 1)$$

*and then showing that $F$ has the properties of the thermodynamic free* energy (of Helmholtz). We must, however, first consider more carefully than hitherto the dependence of $K(T)$ on the volume. Up to the present we have taken as zero of energy the energy of the assembly with all its modes in the lowest quantum state. But if, as we know to be the case, the volume of the crystal varies with the temperature, this state of zero energy will also be shifted. We must now use a true standard state independent of temperature for the energy zero, and we therefore choose the state of infinite separation of the atoms of the crystal, each atom being in some specified normal state. The energy of the crystal in its state of lowest permissible energy will henceforth be denoted by $-N\chi$, so that the value of $\chi$ is positive. For a macroscopic crystal it is physically obvious that the energy of the crystal will be proportional to the number of atoms $N$, and so for a regular crystal subjected to a uniform pressure, $\chi$ will be determined by $V/N$ the volume per atom. The residual energies of the lowest vibrational states of the normal modes are included in $-N\chi$, that of a mode with frequency $\nu$ being $\frac{1}{2}h\nu$.

When we use this new energy zero we have for $K(T)$ instead of (405, 1)

$$\log K(T) = \frac{N\chi}{kT} - N\int_0^\infty g(\nu)\log(1-e^{-h\nu/kT})\,d\nu + N\log v_0\rho. \quad (408, 2)$$

The distribution function $g(\nu)$ will strictly depend on $N$ and $V$, but for given values of $V/N$, or more generally for given values of size and shape of the basal cell, it can be proved to approach a limiting form for large $N$. It is only this limiting form, necessarily independent of $N$ except in the form $V/N$, which we need consider. It is therefore natural to introduce the volume per atom $V$ defined by

$$V = NV, \quad (408, 3)$$

and to introduce a function $K(T, V)$ defined by

$$K(T, N, V) = [\kappa(T, V)]^N. \quad (408, 4)$$

It is convenient to refer to $\kappa(T, V)$ as the partition function per atom in the crystal. We have then

$$\log\kappa(T, V) = \frac{\chi}{kT} - \int_0^\infty g(\nu)\log(1-e^{-h\nu/kT})\,d\nu + \log v_0\rho, \quad (408, 5)$$

and formula (1) which defines $F$ becomes

$$F = -NkT\log\kappa(T, V) = -NkT\log\kappa(T, V/N). \quad (408, 6)$$

We have now to verify that $F$ has the properties of the free energy, that is to say of the thermodynamic potential for the independent variables $T$, $V$, $N$. We therefore differentiate $F/T$ regarded as a function of $T$, $V$, $N$.

We obtain

$$d(F/T) = -Nk\left(\frac{\partial \log \kappa}{\partial T}\right)_{V,N} dT - Nk\left(\frac{\partial \log \kappa}{\partial V}\right)_{T,N} dV$$
$$-k\left\{\log \kappa + N\left(\frac{\partial \log \kappa}{\partial N}\right)_{T,V}\right\} dN. \qquad (408, 7)$$

But according to (407, 2) and (4) we have

$$\bar{E} = NkT^2\left(\frac{\partial \log \kappa}{\partial T}\right)_{V,N}, \qquad (408, 8)$$

and, since the only geometrical coordinate $x$ is $V$ and the corresponding generalized force is the pressure $P$, (407, 6) becomes, when we use (4),

$$P = NkT\left(\frac{\partial \log \kappa}{\partial V}\right)_{T,N}. \qquad (408, 9)$$

Hence by comparing (8) and (9) with (7) we derive

$$d(F/T) = -\frac{\bar{E}}{T^2} dT - \frac{P}{T} dV - k\left\{\log \kappa + N\left(\frac{\partial \log \kappa}{\partial N}\right)_{T,V}\right\} dN. \quad (408, 10)$$

If we identify the average energy $\bar{E}$ of the crystal with the thermodynamic total energy $E$, we see that the dependence of $F$ on $T$ is just what it should be if $F$ is the free energy. The dependence of free energy on the volume is also correctly given by (10). We can then complete the identification of $F$ with the free energy by assuming the partial potential $\mu$ to be given by

$$\mu = \left(\frac{\partial F}{\partial N}\right)_{T,V} = -kT\left\{\log \kappa + N\left(\frac{\partial \log \kappa}{\partial N}\right)_{T,V}\right\}. \quad (408, 11)$$

But since $\kappa$ depends on $N$ only through $V/N = v$, we have

$$-NkT\left(\frac{\partial \log \kappa}{\partial N}\right)_{T,V} = kTv\left(\frac{\partial \log \kappa}{\partial v}\right)_{T,N} = Pv, \qquad (408, 12)$$

using (9). Hence substituting (12) into (11) we obtain

$$\mu = -kT \log \kappa + Pv. \qquad (408, 13)$$

For the contribution $f$ of each atom to the free energy we have

$$f = \mu - Pv = -kT \log \kappa, \qquad (408, 14)$$

in agreement with (6).

We see then that if we take $F$ defined by (6) to be the free energy of the crystal, the dependence of $F$ on $T$ and $V$ is correct. The dependence on $N$, which leads to (13), is as a matter of fact also correct, but proof of this must be deferred to Chapter v, where we consider variations in $N$ due to evapora-

tion and condensation. Until we introduce such considerations, variations of $N$ are irrelevant. Meanwhile we shall assume the free energy of a crystal to be statistically defined by (6).

**§ 409. Thermodynamic functions according to Debye's approximation.** We return now to Debye's approximation, and shall combine it with the formulae of the preceding section for the thermodynamic properties, confining attention to regular crystals subjected to a uniform pressure. On Debye's approximation the frequencies of the normal modes are distributed according to (404, 7), with $\nu_D$ or $\Theta_D$ depending on $V = V/N$, and so the total contribution of their residual energies to $-\chi$ is

$$\int_0^{\nu_D} \frac{9\nu^2}{\nu_D^3} \tfrac{1}{2}h\nu \, d\nu = \tfrac{9}{8}h\nu_D = \tfrac{9}{8}k\Theta_D. \tag{409, 1}$$

Substituting from (404, 7) into (408, 5) we obtain

$$\begin{aligned}\log \kappa(T,V) &= \frac{\chi}{kT} - \frac{9}{\nu_D^3}\int_0^{\nu_D} \nu^2 \log(1 - e^{-h\nu/kT})\, d\nu + \log v_0 \rho \\ &= \frac{\chi}{kT} - 9\frac{T^3}{\Theta_D^3}\int_0^{\Theta_D/T} \xi^2 \log(1 - e^{-\xi})\, d\xi + \log v_0\rho. \end{aligned} \tag{409, 2}$$

Consequently for the free energy of the crystal we have by (408, 14) and (2)

$$\begin{aligned} F = \frac{F}{N} &= -\chi + 9k\frac{T^4}{\Theta_D^3}\int_0^{\Theta_D/T} \xi^2 \log(1-e^{-\xi})\, d\xi - kT\log v_0 \rho \\ &= -\chi + 3kT\log(1 - e^{-\Theta_D/T}) - \frac{3kT^4}{\Theta_D^3}\int_0^{\Theta_D/T} \frac{\xi^3}{e^{\xi}-1}\, d\xi - kT\log v_0\rho, \end{aligned} \tag{409, 3}$$

using integration by parts.

For the total energy, remembering that $\chi$ and $\Theta_D$ are functions of $T$ and $V = V/N$ only, we have

$$\begin{aligned} \frac{E}{N} &= -\frac{T^2}{N}\left(\frac{\partial[F/T]}{\partial T}\right)_{V,N} = kT^2\left(\frac{\partial \log \kappa}{\partial T}\right)_V \\ &= -\chi + 9k\frac{T^4}{\Theta_D^3}\left\{\left(\frac{\Theta_D}{T}\right)^3 \log(1-e^{-\Theta_D/T})\right\} - 9k\frac{T^4}{\Theta_D^3}\int_0^{\Theta_D/T} 3\xi^2\log(1-e^{\xi})\, d\xi \\ &= -\chi + 9k\frac{T^4}{\Theta_D^3}\int_0^{\Theta_D/T}\frac{\xi^3}{e^{\xi}-1}\, d\xi, \end{aligned} \tag{409, 4}$$

using integration by parts.

We can readily obtain simple approximations to these formulae when $T/\Theta_D$ is large or small. For high temperatures, $T \gg \Theta_D$, we expand $\xi^3/(e^{\xi}-1)$ in power series in $\xi$ and integrate term by term, and expand $\log(1-e^{-\Theta_D/T})$

in a power series in $\Theta_D/T$. We thus obtain

$$F = \frac{F}{N} = -\chi + 3kT\left\{\log\frac{\Theta_D}{T} - \frac{1}{3} - \frac{3}{8}\frac{\Theta_D}{T} + \frac{1}{40}\left(\frac{\Theta_D}{T}\right)^2 + O\left(\frac{\Theta_D}{T}\right)^4\right\} - kT\log v_0\rho$$

$$= (-\chi - \tfrac{9}{8}k\Theta_D) + 3kT\left\{\log\frac{\Theta_D}{T} - \frac{1}{3} + \frac{1}{40}\left(\frac{\Theta_D}{T}\right)^2 + O\left(\frac{\Theta_D}{T}\right)^4\right\} - kT\log v_0\rho$$

$$(T \gg \Theta_D), \quad (409, 5)$$

$$\frac{E}{N} = (-\chi - \tfrac{9}{8}k\Theta_D) + 3kT\left\{1 + \frac{1}{20}\left(\frac{\Theta_D}{T}\right)^2 + O\left(\frac{\Theta_D}{T}\right)^4\right\} \quad (T \gg \Theta_D). \quad (409, 6)$$

It will be noted that the term in $\Theta_D$ cancels the residual energy in $-\chi$ and that there is no term in $(\Theta_D/T)^3$.

When the temperature is low we replace $\int_0^{\Theta_D/T}$ by $\int_0^\infty - \int_{\Theta_D/T}^\infty$, evaluate the infinite integral by (403, 2), and obtain an approximation to the second integral by integration by parts. We find

$$F = \frac{F}{N} = -\chi - kT\log v_0\rho - 3kT\left\{\frac{\pi^4}{15}\frac{T^3}{\Theta_D^3} - 3\frac{T}{\Theta_D}e^{-\Theta_D/T} + O\left(\frac{T^2}{\Theta_D^2}e^{-\Theta_D/T}\right)\right\}$$

$$(T \ll \Theta_D), \quad (409, 7)$$

$$E = \frac{E}{N} = -\chi + 3kT\left\{\frac{\pi^4}{5}\frac{T^3}{\Theta_D^3} - 3e^{-\Theta_D/T} + O\left(\frac{T}{\Theta_D}e^{-\Theta_D/T}\right)\right\} \quad (T \ll \Theta_D). \quad (409, 8)$$

**§ 410. Heat capacities of atomic crystals.** We obtain the atomic heat capacity at constant volume for an atomic crystal by differentiating the energy with respect to the temperature, keeping $V$, $N$ constant; $\chi$ and $\Theta_D$ being functions of $V$ only, thus remain constant also. Using Debye's approximation (409, 4) for the energy, we obtain for the atomic heat capacity $C_V$

$$C_V = \frac{\partial}{\partial T}\left\{9kT\frac{T^3}{\Theta_D^3}\int_0^{\Theta_D/T}\frac{\xi^3}{e^\xi - 1}d\xi\right\}. \quad (410, 1)$$

The forms of $C_V$ for high and low temperatures are obtained directly from the approximations to $E$ given in the preceding paragraph. For high temperatures we have by (409, 6)

$$C_V = 3k\left\{1 - \frac{1}{20}\frac{\Theta_D^2}{T^2} + O\left(\frac{\Theta_D}{T}\right)^4\right\} \quad (T \gg \Theta_D), \quad (410, 2)$$

while for low temperatures we have by (409, 8)

$$C_V = 3k\left\{\frac{4\pi^4}{5}\frac{T^3}{\Theta_D^3} + O\left(\frac{T}{\Theta_D}e^{-\Theta_D/T}\right)\right\} \quad (T \ll \Theta_D). \quad (410, 3)$$

**§ 411. Comparison of Debye's approximations with experiment.*** At high temperatures Debye's $c_V$ has the value $3k$, and this should be accurate (according to this theory) to within $\frac{1}{2}$ % so long as $T > 3\Theta_D$. This is an example of the theorem of equipartition, and should actually hold more widely than Debye's theory, remaining true when $g(\nu)$ differs widely from $\alpha\nu^2$, so long as $T > 3h\nu_{\max}/k$. The equality $c_V = 3k$ corresponds to a heat capacity per gram atom of 6 cal./deg. This is an improved form of the old rule of Dulong and Petit, which states that the gram-atomic heat capacity is approximately 6·4 cal./deg. for all elements in the solid state. The heat capacity referred to in this empirical rule is, however, $c_P$, the heat capacity at constant pressure. The heat capacities for any substance are connected by the thermodynamic formula†

$$c_P - c_V = T\left(\frac{\partial V}{\partial T}\right)_P\left(\frac{\partial P}{\partial T}\right)_V$$

$$= -T\left(\frac{\partial V}{\partial T}\right)_P^2\bigg/\left(\frac{\partial V}{\partial P}\right)_T = \frac{\alpha^2 VT}{\beta}, \qquad (411, 1)$$

where $\alpha$ is the coefficient of (cubical) thermal expansion, and $\beta$ the isothermal compressibility. The reduction from $\mathsf{N}c_P$ to $\mathsf{N}c_V$ has an average value 0·4 cal./deg. gram-atom, so that Dulong and Petit's empirical rule reduces to $\mathsf{N}c_V \simeq 6$ cal./deg. gram-atom, in agreement with the theoretical value $3R$ for high temperatures. When the correction (1) is applied accurately to elements and compounds in solid form, the value $3R$ is found to hold accurately for $\mathsf{N}c_V$ for temperatures which are sufficiently high—not, however, too high since then the approximation of harmonic modes becomes inadequate. Certain metals, notably the transition metals, are exceptions, because they have important electronic contributions, which have here been left out of account.

At low temperatures $c_V$ should according to Debye's approximation vary as $T^3$, with deviations of at most 2 % so long as $T < \Theta_D/10$. This temperature dependence has been found for many substances, of which typical examples are given in Table 1. For other substances the constancy of $c_V/T^3$ is apparently poor, because the temperatures are not low enough for the important normal modes to be distributed according to the assumed $\alpha\nu^2$ law. It has been shown in fact by Blackman's investigations that the true $T^3$-law can be expected to hold only at very low temperatures indeed, and that many of the apparent $T^3$-regions are accidental, because $c_V$ deviates again from this law at lower temperatures and only settles down to a final $T^3$-variation at temperatures still lower. In fact for metals one can hardly

* The experimental data referred to in this section and in § 414, when no other reference is given, are taken from Schrodinger, *Physikal. Zeit.* **20**, 420, 450, 474, 497, 523 (1919). This applies in particular to the data of Tables 1, 3, 8 and of Fig. 2.

† See, for example, *M.T.* p. 36.

expect a true $T^3$-region ever to be reached, since, before it is, contributions by free electrons (§ 1110) may become dominant with a variation like $T$, which will depress sharply the value of $\Theta_D$ derived from the observations.

TABLE 1

*The $T^3$-law for $C_V$ at low temperatures*

| Temp. °K. | $\mathbf{N}C_V$ cal./g. atom | $10^2(\mathbf{N}C_V)^{\frac{1}{3}}/T$ |
|---|---|---|
| | Copper | |
| 14·51 | 0·0390 | 2·35 |
| 15·60 | 0·0506 | 2·37 |
| 17·50 | 0·0726 | 2·39 |
| 18·89 | 0·0930 | 2·40 |
| 20·20 | 0·1155 | 2·42 |
| 21·50 | 0·1410 | 2·42 |
| 23·5 | 0·22 | 2·57 |
| 25·37 | 0·234 | 2·43 |
| 27·7 | 0·32 | 2·47 |
| | Iron | |
| 32·0 | 0·152 | 1·67 |
| 33·1 | 0·177 | 1·70 |
| 35·2 | 0·244 | 1·77 |
| 38·1 | 0·288 | 1·73 |
| 42·0 | 0·325 | 1·64 |
| 46·9 | 0·522 | 1·71 |
| | Aluminium | |
| 19·1 | 0·066 | 2·12 |
| 23·6 | 0·110 | 2·03 |
| 27·2 | 0·162 | 2·01 |
| 32·4 | 0·25 | 1·95 |
| 33·5 | 0·301 | 2·00 |
| 35·1 | 0·33 | 1·97 |

At intermediate temperatures Debye's value for $C_V$ cannot be expressed in any simpler form than (410, 1). It is, however, evident that Debye's $C_V/k$, like $E/NT$, is a universal function of $\Theta_D/T$. This theoretical value of $C_V/3k$ as a function of $\Theta_D/T$ is given in Table 2. That this law of corresponding states for $C_V$ is in fact roughly true for elements, and many simple compounds, is well shown* by the data plotted in Fig. 2 for eighteen simple substances, particulars being given in Table 3. For each substance in Fig. 2 the value of $\Theta_D$ has been chosen to give the best general fit between the observations and Debye's formula (410, 1). The general agreement there shown indicates that, for these and many other substances, the deviations of $g(\nu)$ from $\alpha\nu^2$ are not sufficiently violent to give a marked nonconformity with Debye's theory over a limited temperature range, when the theory and the observations are fitted in this way.

* The applicability of the formula to compounds will be discussed below in § 414.

TABLE 2

*$C_V/3k$ as a function of $\Theta_D/T$ according to Debye*

Reference: J. A. Beattie, *Journal of Mathematics and Physics* (Mass. Inst. Tech.), **6**, 1 (1926–27)

| $\Theta_D/T$ | 0·0 | 0·1 | 0·2 | 0·3 | 0·4 | 0·5 | 0·6 | 0·7 | 0·8 | 0·9 | 1·0 |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 0·0 | 1·0000 | 0·9995 | 0·9980 | 0·9955 | 0·9920 | 0·9876 | 0·9822 | 0·9759 | 0·9687 | 0·9606 | 0·9517 |
| 1·0 | 0·9517 | 0·9420 | 0·9315 | 0·9203 | 0·9085 | 0·8960 | 0·8828 | 0·8692 | 0·8550 | 0·8404 | 0·8254 |
| 2·0 | 0·8254 | 0·8100 | 0·7943 | 0·7784 | 0·7622 | 0·7459 | 0·7294 | 0·7128 | 0·6961 | 0·6794 | 0·6628 |
| 3·0 | 0·6628 | 0·6461 | 0·6296 | 0·6131 | 0·5968 | 0·5807 | 0·5647 | 0·5490 | 0·5334 | 0·5181 | 0·5031 |
| 4·0 | 0·5031 | 0·4883 | 0·4738 | 0·4595 | 0·4456 | 0·4320 | 0·4187 | 0·4057 | 0·3930 | 0·3807 | 0·3686 |
| 5·0 | 0·3686 | 0·3569 | 0·3455 | 0·3345 | 0·3237 | 0·3133 | 0·3031 | 0·2933 | 0·2838 | 0·2745 | 0·2656 |
| 6·0 | 0·2656 | 0·2569 | 0·2486 | 0·2405 | 0·2326 | 0·2251 | 0·2177 | 0·2107 | 0·2038 | 0·1972 | 0·1909 |
| 7·0 | 0·1909 | 0·1847 | 0·1788 | 0·1730 | 0·1675 | 0·1622 | 0·1570 | 0·1521 | 0·1473 | 0·1426 | 0·1382 |
| 8·0 | 0·1382 | 0·1339 | 0·1297 | 0·1257 | 0·1219 | 0·1182 | 0·1146 | 0·1111 | 0·1078 | 0·1046 | 0·1015 |
| 9·0 | 0·1015 | 0·09847 | 0·09558 | 0·09280 | 0·09011 | 0·08751 | 0·08500 | 0·08259 | 0·08025 | 0·07800 | 0·07582 |
| 10·0 | 0·07582 | 0·07372 | 0·07169 | 0·06973 | 0·06783 | 0·06600 | 0·06424 | 0·06253 | 0·06087 | 0·05928 | 0·05773 |
| 11·0 | 0·05773 | 0·05624 | 0·05479 | 0·05339 | 0·05204 | 0·05073 | 0·04946 | 0·04823 | 0·04705 | 0·04590 | 0·04478 |
| 12·0 | 0·04478 | 0·04370 | 0·04265 | 0·04164 | 0·04066 | 0·03970 | 0·03878 | 0·03788 | 0·03701 | 0·03617 | 0·03585 |
| 13·0 | 0·03535 | 0·03455 | 0·03378 | 0·03303 | 0·03230 | 0·03160 | 0·03091 | 0·03024 | 0·02959 | 0·02896 | 0·02835 |
| 14·0 | 0·02835 | 0·02776 | 0·02718 | 0·02661 | 0·02607 | 0·02553 | 0·02501 | 0·02451 | 0·02402 | 0·02354 | 0·02307 |
| 15·0 | 0·02307 | 0·02262 | 0·02218 | 0·02174 | 0·02132 | 0·02092 | 0·02052 | 0·02013 | 0·01975 | 0·01938 | 0·01902 |

| $\Theta_D/T$ | 0·0 | $\Theta_D/T$ | 0·0 |
|---|---|---|---|
| 16·0 | 0·01902 | 21·0 | 0·008415 |
| 17·0 | 0·01586 | 22·0 | 0·007318 |
| 18·0 | 0·01336 | 23·0 | 0·006405 |
| 19·0 | 0·01136 | 24·0 | 0·005637 |
| 20·0 | 0·009741 | | |

$$\frac{C_V}{3k} = \frac{77{\cdot}92727}{(\Theta_D/T)^3} \quad \text{when} \quad \Theta_D/T > 24$$

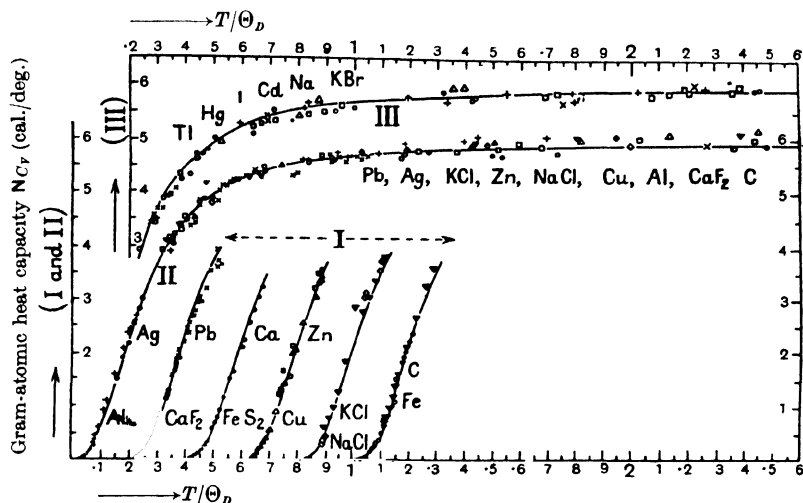



Fig. 2. The gram atomic heat capacities of various solids as functions of $T/\Theta_D$.

TABLE 3

*Data for Fig. 2, studying the law of corresponding states*

| Substance | Chemical symbol | Temperature range °K. | $\Theta_D$ | Points in Fig. 2 | | |
|---|---|---|---|---|---|---|
| | | | | Curves | | |
| | | | | I | II | III |
| Lead | Pb | 14–573 | 88 | × | × | |
| Thallium | Tl | 23–301 | 96 | | | ○ |
| Mercury | Hg | 31–232 | 97 | | | □ |
| Iodine | I | 22–298 | 106 | | | × |
| Cadmium | Cd | 50–380 | 168 | | | + |
| Sodium | Na | 50–240* | 172 | | | △ |
| Potassium bromide | KBr | 79–417 | 177 | | | ● |
| Silver | Ag | 35–873 | 215 | | ● | |
| Calcium | Ca | 22– 62 | 226 | ○ | | |
| Sylvine | KCl | 23–550 | 230 | ▽ | ▽ | |
| Zinc | Zn | 33–673 | 235 | □ | □ | |
| Rocksalt | NaCl | 25–664 | 281 | ◇ | ◇ | |
| Copper | Cu | 14–773* | 315 | △ | △ | |
| Aluminium | Al | 19–773 | 398 | | + | |
| Iron | Fe | 32–95* | 453 | ○ | | |
| Fluorspar | $CaF_2$ | 17–328 | 474 | ○ | ○ | |
| Iron pyrites | $FeS_2$ | 22–57* | 645 | + | | |
| Diamond | C | 30–1169 | 1860 | ▼ | ▼ | |

* For Na, Cu, Fe, $FeS_2$, $C_V$ rises *above* the curve after these temperatures.

A more sensitive test of Debye's theory, and hence of the deviations between $g(\nu)$ and $\alpha\nu^2$, is provided by the following procedure. The heat capacity $C_V$, derived from the observations for any given temperature, is compared with Debye's value, and made to agree exactly by the proper choice of $\Theta_D$. The observations are thus reduced to a set of "observed" values of $\Theta_D$ as a function of $T$. This function would of course be constant, if Debye's approximation were exact, except for the variation of $\Theta_D$ itself with temperature, even in Debye's theory, due to the thermal changes in the elastic constants referred to at the close of this section. This variation in $\Theta_D$ is, however, never more than a small percentage change, and always in the direction of a decrease with increasing temperature. The actual

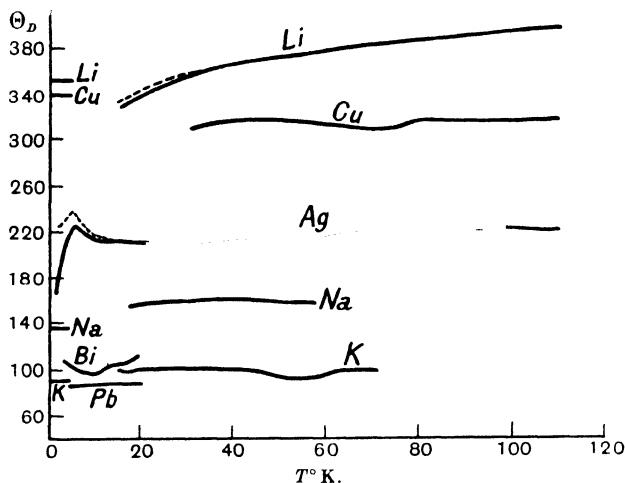



Fig. 3. Experimental $\Theta_D$, $T$ curves for various metals. The dotted curves show the values after subtraction of the electronic contributions (see Chapter XI) to the heat capacity.

variations in $\Theta_D$ are mainly, and, for simple substances, almost entirely, due to the failure of Debye's $\alpha\nu^2$ approximation. Examples of such determinations of $\Theta_D(T)$ are shown in Fig. 3 due to Mott and Jones.* Lithium is particularly noteworthy, as the variations in $\Theta_D$ are large and we have no reason whatever to attribute them to any other cause. A similar analysis of the data for diamond in a higher temperature range is given in Table 4.

The great initial successes of Debye's theory have tended somewhat to obscure the essentially approximate nature of the $g(\nu)$ used by him. As a result, values of $C_V$ have been held to be anomalous and to require a special explanation, when in fact the only unusual feature is a somewhat more marked departure of $g(\nu)$ from $\alpha\nu^2$ than usual. A great variety of curves of

* Mott and Jones, *Properties of Metals and Alloys* (Oxford, 1936).

heat capacity are possible for values of $g(\nu)$, possible for an actual lattice.[A] A specimen of the behaviour of $\Theta_D(T)$ for a simple cubic lattice is shown in Fig. 4. There is, however, one thing that the heat capacity of lattice vibrations can never do, so long as the assumption of simple harmonic modes is

TABLE 4

*Observed values of $\Theta_D(T)$ for diamond**

| C (diamond) | | C (diamond) | |
|---|---|---|---|
| $T°$ K. | $\Theta_D(T)$ | $T°$ K. | $\Theta_D(T)$ |
| 70·2 | 1930 | 173 3 | 1833 |
| 75·4 | 1890 | 200·9 | 1818 |
| 81·6 | 1900 | 211·8 | 1820 |
| 88·6 | 1930 | 231·1 | 1817 |
| 96·7 | 1920 | 252 4 | 1840 |
| 105 1 | 1900 | 276·6 | 1855 |
| 125 3 | 1874 | 288·0 | 1865 |
| 153·7 | 1845 | | |

* Pitzer, *J Chem Phys* **6**, 68 (1938)

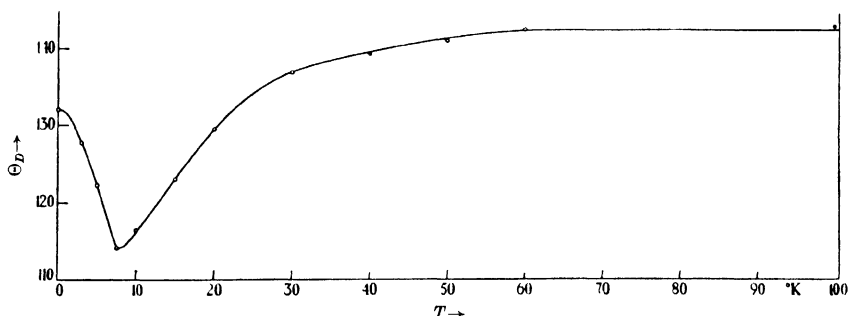



Fig. 4 Debye's $\Theta_D$ as a function of the temperature for a simple cubic lattice for a ratio 0 05 of the force constant between next nearest neighbours to the force constant between nearest neighbours.

legitimate, it can never decrease as $T$ increases. If we calculate $C_V$ using (404, 1), instead of Debye's approximation (404, 8), we find

$$C_V = k \int_0^{\nu_{max}} g(\nu) \left[\frac{\frac{1}{2}h\nu/kT}{\sinh \frac{1}{2}h\nu/kT}\right]^2 d\nu. \qquad (411, 2)$$

But the function $x/\sinh x$ steadily decreases from 1 to 0 as $x$ increases from zero to infinity. The integrand of $C_V$ therefore increases as $T$ increases for each fixed value of $\nu$, so that $C_V$ itself can never decrease. It follows that if any observed value of $C_V$ decreases in any range of values of $T$, the decrease

[A] See appendix, § A2.

must occur in some contribution which is not due to lattice vibrations, and some special explanation is called for.

As a final test of the theory we may compare the values of $\Theta_D$, which fit the experimental $C_V$-$T$ curve for a given substance, with the values calculated from the elastic constants. There are two such constants for an isotropic solid, which may be taken to be the compressibility $\beta$, and Poisson's ratio $\sigma$. In terms of these the velocities of sound $c_l$ and $c_t$ are

$$c_l^2 = \frac{3(1-\sigma)}{(1+\sigma)\beta\rho}, \quad c_t^2 = \frac{3(1-2\sigma)}{2(1+\sigma)\beta\rho}, \qquad (411,3)$$

where $\rho$ is the density. $\Theta_D$ is then given in terms of $\beta$, $\sigma$ and $\rho$ by substituting from (3) into

$$\frac{1}{\Theta_D^3} = \frac{4\pi V}{9N}\frac{k^3}{h^3}\left(\frac{1}{c_l^3}+\frac{2}{c_t^3}\right), \qquad (411,4)$$

obtained by combination of (402, 1), (404, 11). The comparison is shown for four substances in Table 5.

TABLE 5

*Comparison of the values of $\Theta_D$ from heat capacities and from direct calculation from the elastic constants*

| Substance | $\rho$ g./cm.$^3$ | $\beta \times 10^{12}$ cm.$^2$/dynes | $\sigma$ | $\Theta_D$ from heat capacity | $\Theta_D$ from elastic constants |
|---|---|---|---|---|---|
| Al | 2·71 | 1·36 | 0·337 | 398 | 402 |
| Cu | 8·96 | 0·74 | 0·334 | 315 | 332 |
| Ag | 10·53 | 0·92 | 0·379 | 215 | 214 |
| Pb | 11·32 | 2·0 | 0·446 | 88 | 73 |

Table taken from Born, *Atomtheorie des festen Zustandes* (Berlin, 1923).

In view of the approximate nature of the theory, as applied to the heat capacity at normal temperatures, it is hardly worth while discussing how far such good agreement is to be anticipated. At low temperatures, however, the Debye theory should be exact, and the agreement should be good. There are, however, no direct measurements of the elastic constants at low temperatures, so the best that can be done is to extrapolate from measurements at ordinary temperatures, using estimates due to Grüneisen.* The values of $\Theta_D$ derived thus and in various other ways are collected† and compared in Table 6.

The agreement between the low temperature $\Theta_D$ values should hold generally for compounds, not merely for elements, as will be made clear in

* Grüneisen and Hoyer, *Ann. d. Physik*, **22**, 665 footnote (1935).

† For references see Mott and Jones, *Properties of Metals and Alloys*, Chapter I (Oxford, 1936).

§413. It is therefore perhaps worth while to extend this part of the comparison to other substances. In Table 7 data are given for elements which have a crystal lattice other than cubic, and for simple compounds.

TABLE 6

*A comparison of the values of $\Theta_D$ derived by various methods*

| Substance | C (diamond) | Fe | Al | Cu | Ag* | W |
|---|---|---|---|---|---|---|
| $\Theta_D$ from general $C_V$-$T$ curve | 1860 | 453 | 398 | 315 | 215 | 305 |
| $\Theta_D$ from $T^3$ law at temperatures less than $\Theta_D/12$ | 2230 | 434 to 392 | $\simeq$ 385 | 316 to 330 | 212 to 225 | $\simeq$ 337 |
| $\Theta_D$ from elastic data at 290° K. | — | 461 | 394 | 342 | 212 | 384 |
| $\Theta_D$ from estimated values of elastic constants at 0° K. | — | 468 | 406 | 351 | 218 | 390 |

* Low temperature values below 4 are seriously affected by electronic contributions and are therefore omitted here.

TABLE 7

*Further comparisons of the values of $\Theta_D$ at low temperatures derived from heat capacities and elastic constants*

| Substance | Zn | Cd | NaCl | KCl | MgO | ZnS |
|---|---|---|---|---|---|---|
| $\Theta_D$ from $T^3$ law for heat capacities at temperatures less than $\Theta_D/12$ | 200<br>270<br>163 | $\simeq$ 130 | 275<br>308 | 212<br>237<br>220 | 750<br>890 | $\simeq$ 260 |
| $\Theta_D$ from estimated values of elastic constants at 0° K | 320 | 200 | 320 | 246 | 946 | 336 |

On the whole, there appears to be reasonably good agreement between the values of $\Theta_D$ calculated from the $T^3$ law and from the elastic constants. The electronic contributions to the heat capacity may depress $\Theta_D$ but it is doubtful if they can account for the whole of the discrepancy for W, Zn and Cd. For NaCl and KCl, where no such terms can arise, the discrepancy is small and probably not significant. For ZnS the $\Theta_D$ value from the heat capacity might very likely rise again and *remove the discrepancy*, if the measurements were extended to lower temperatures. In general the largest values of $\Theta_D$ from the heat capacities and those in best agreement with $\Theta_D$ from the elastic constants come from the lowest (very low) temperatures.

**§412. Equation of state of crystal (Debye's approximation).** Since the pressure is the generalized force corresponding to the volume, we can obtain its value by differentiating the free energy with respect to the

volume. Using (409, 3), we obtain

$$P = -\frac{\partial F}{\partial V} = kT\frac{\partial(N\log\kappa)}{\partial V} = kT\frac{\partial\log\kappa}{\partial V}$$

$$= \frac{\partial\chi}{\partial V} + kT\frac{\partial\Theta_D}{\partial V}\frac{\partial}{\partial\Theta_D}\left[9\frac{T^3}{\Theta_D^3}\int_0^{\Theta_D/T}\xi^2\log(1-e^{-\xi})\,d\xi\right]$$

$$= \frac{\partial\chi}{\partial V} - \frac{9kT^4}{\Theta_D^4}\frac{\partial\Theta_D}{\partial V}\int_0^{\Theta_D/T}\frac{\xi^3}{e^{\xi}-1}\,d\xi. \qquad (412, 1)$$

This formula may be considered as the equation of state of the crystal. It can be useful only if we know how $\chi$ and $\Theta_D$ depend on $V$, and for this we should require a fairly detailed knowledge of the interatomic forces. We shall therefore make no direct use of (1).

Formulae (408, 11) for the partial potential $\mu$ gives us

$$\mu = -kT\left\{\log\kappa + N\left(\frac{\partial\log\kappa}{\partial N}\right)_V\right\} = -kT\left\{\log\kappa - V\frac{\partial\log\kappa}{\partial V}\right\}. \qquad (412, 2)$$

Comparing (2) with (408, 6) and (1), we see that the thermodynamic relation

$$F + PV = F + PNV = N\mu \qquad (412, 3)$$

is satisfied identically.

**§ 413. Crystals composed of molecules.** The formulae of Debye's theory are directly applicable only to crystals containing a single kind of atom. Let us now consider crystals containing one or more elements, having in all cases the atoms grouped into molecules. For a crystal of this type, containing $N$ molecules each composed of $s$ atoms, we can evidently obtain an approximation to the normal modes by assuming $3N$ modes with frequencies distributed according to Debye's theory, and treating the remaining $3N(s-1)$ modes as internal degrees of freedom of the molecules, to a first approximation unaffected by the packing of the molecules into the crystal lattice. We then have a partition function $K(T)$ for the crystal of the form

$$\log K(T) = \frac{N\chi}{kT} - 9N\frac{T^3}{\Theta_D^3}\int_0^{\Theta_D/T}\xi^2\log(1-e^{-\xi})\,d\xi + N\log j(T), \quad (413, 1)$$

where $j(T)$ is the partition function for the internal degrees of freedom of the molecule, including the electronic motions and nuclear spins. Usually these internal degrees of freedom, $3(s-1)$ in number per molecule apart from the electronic motions, may be regarded approximately as simple harmonic vibrations of the same frequency for each molecule in the crystal. Their contributions to the thermodynamic functions are therefore often described as Einstein terms. If the frequencies of these vibrations are

denoted by $k\Theta_4/h, k\Theta_5/h, \ldots, k\Theta_{3s}/h$, or in general by $k\Theta_i/h$, then the partition function for the crystal takes the form

$$\log K(T) = \frac{N\chi}{kT} - 9N\frac{T^3}{\Theta_D^3}\int_0^{\Theta_D/T} \xi^2 \log(1-e^{-\xi})\,d\xi$$
$$- N\sum_{i=4}^{3s}\log(1-e^{-\Theta_i/T}) + N\log v_0 \Pi\rho, \qquad (413, 2)$$

where $\Pi\rho$ denotes the product of the nuclear spin weights in each molecule.* The corresponding formulae for the free energy and total energy are

$$\frac{F}{N} = -\chi + 9k\frac{T^4}{\Theta_D^3}\int_0^{\Theta_D/T} \xi^2\log(1-e^{-\xi})\,d\xi + kT\sum_{i=4}^{3s}\log(1-e^{-\Theta_i/T}) - kT\log v_0\Pi\rho, \qquad (413, 3)$$

$$\frac{E}{N} = -\chi + 9k\frac{T^4}{\Theta_D^3}\int_0^{\Theta_D/T}\frac{\xi^3}{e^{\xi}-1}\,d\xi + kT\sum_{i=4}^{3s}\frac{\Theta_i/T}{e^{\Theta_i/T}-1}. \qquad (413, 4)$$

By differentiating (4) with respect to $T$ we can obtain a formula for the heat capacity.

It may happen that one, two or three of the internal degrees of freedom of the molecule in the crystal are described to a better approximation as rotations than as harmonic vibrations. This possibility was first suggested by Simon† and investigated by Pauling,‡ who also considered the transition from an almost free rotation to a vibration, as the temperature is lowered and the potential energy of orientation becomes more important compared with $kT$. Pauling gave reasons for supposing that free rotation is the better approximation in the case of $H_2$. For other molecules or radicals containing only one atom other than H, such as ClH, $CH_4$, $NH_4^+$, the motion is effectively a rotation at high temperatures, but a vibration (libration) at low temperatures. There is a more or less sharp transition in a short temperature range. When the free rotation is a better approximation than a vibration, one, two or three Einstein terms must be replaced by the partition function for a one, two or three-dimensional rotator. We shall have occasion to refer to this again in Chapter V.

**§414. Crystals with ionic or complex lattices.** We have already mentioned the work of Born in analysing the normal modes of crystals, on which Blackman's advances have been based. It will be convenient in closing this elementary account of crystal partition functions to give some account of his results, as they show how the analysis given above is to be extended to more complex crystals.

If all the atoms in a crystal are not of the same type, or of the same type but

* In certain cases an extra term $N\log o$ ($o$ constant) must be introduced. See Chapter V, especially §§ 516 sqq.

† Simon and Simson, *Zeit. Phys.* **21**, 176 (1924). ‡ Pauling, *Phys. Rev.* **36**, 430 (1930).

not all similarly situated in the lattice, they must be grouped into elementary cells containing $s$ atoms each, the cells being identical repetitions of one another. *A crystal of $N$ unit cells, containing $sN$ atoms, can then be shown to possess $3s$ distinct sets of normal modes and frequencies. The wave numbers (reciprocal wave lengths) of each set are distributed uniformly in a three-dimensional space, in which spherical polar coordinates represent wave number and direction of the normal to the corresponding wave front.* This result of Born's is exact, but of no use for computing the partition function until the connection between wave number and frequency is established. It is here that exact analysis is difficult, and that recent progress has been made by Blackman, with results in simple cases which we have already examined. The approximate procedure used by Born is to divide the sets of frequencies into two types, commonly referred to as acoustical and optical (infra-red) respectively. The essential feature of a set of acoustical modes is that the frequency $\nu_a$ tends to zero when the wave length $\lambda_a$ becomes large according to the formula

$$\nu_a = c_a/\lambda_a, \qquad (414, 1)$$

where $c_a$ is the velocity of sound for long waves. The velocity $c_a$ is not strictly independent of $\lambda_a$, but this variation is ignored by Born for this type of mode, which is equivalent to using Debye's approximation for these types. The essential feature of an optical set of modes is that the frequency tends to a non-zero limit $\nu_i$ as the wave length increases. The frequency is not strictly independent of wave length, but Born's approximation is to ignore its variations compared with $\nu_i$. Each such set is therefore assumed to consist of $N$ identical frequencies. This is Einstein's approximation, the same approximation as was suggested by the wider discussion of § 413. Each set of $N$ acoustical modes, to this rough approximation, will contribute a Debye term, and each set of $N$ optical modes an Einstein term to the partition function and resulting thermodynamic functions.

It remains to consider how many of the $3s$ sets are acoustical and how many optical, in the sense that their frequencies are roughly represented by Debye or by Einstein approximations. The best answer will depend on the structure of the crystal. We have seen in § 413 that, when each basal cell may really be regarded as a distinct molecule, it is natural to take three acoustical sets (containing $3N$ frequencies in all) and $3(s-1)$ sets each of $N$ equal optical frequencies. For a simple ionic lattice of two atoms of approximately the same mass, such as KCl, it will obviously be a better approximation to assume six sets each of $N$ acoustical frequencies. As the mass difference increases for such a lattice, this approximation becomes worse. In a lattice such as that of $CaCO_3$ we should expect nine of the fifteen sets of modes to be definitely optical with $\nu_i$'s well separated from zero, and three

to be definitely acoustical; it seems not unlikely that the remaining three sets will be of an intermediate nature, with $\nu_i$'s so small that the variations of the frequencies with wave length are comparable with them. In all this analysis it must be remembered that a set of acoustical modes, which must conform to $g(\nu) \sim \alpha\nu^2$ for low frequencies, may deviate more or less widely from this law for higher frequencies.

We may therefore expect the partition functions for any crystal, excluding free rotations of molecules or radicals, to be representable roughly by the product of $3s$ partition functions, of which at least three will be of the Debye type and the remainder of Einstein's. At high temperatures, when $T \gg \Theta$, either type of term contributes $k$ to the heat capacity per cell, while at extremely low temperatures, when $T \ll \Theta$, either type contributes to the heat capacity a term which tends to zero as $T$ tends to zero. It is therefore only in the range where $T$ is comparable with or at least not very much smaller than $\Theta$ that the difference between the two types of terms is important. In practice it is found empirically that for crystals of many simple compounds the heat capacity is adequately reproduced by the simple Debye formula, with three terms per atom and only one $\Theta$ value. This is shown by the inclusion of several compounds in Fig. 2. The $T^3$-law for $C_V$ should also be obeyed at low temperatures by simple compounds. That this is so is suggested by the data in Table 8. It must be admitted however that the

TABLE 8

*The $T^3$-law at low temperatures for simple compounds**

| Temp. °K. | $\mathbf{N}C_V$ cal./mole deg. | $10^2(\mathbf{N}C_V)^{\frac{1}{3}}/T$ |
|---|---|---|
| | Iron pyrites ($FeS_2$) | |
| 27·5 | 0·1095 | 1·75 |
| 29·8 | 0·1385 | 1·74 |
| 32·9 | 0·179 | 1·72 |
| 35·8 | 0·232 | 1·72 |
| 38·3 | 0·295 | 1·74 |
| 42·2 | 0·402 | 1·75 |
| 46·7 | 0 530 | 1·74 |
| 51·7 | 0·712 | 1·74 |
| 54·7 | 0·844 | 1·74 |
| 56·9 | 0 952 | 1·73 |
| | Beryl (BeO) | |
| 76·8 | 0·202 | 0·765 |
| 78·1 | 0·219 | 0·773 |
| 79·3 | 0·226 | 0·769 |
| 80·3 | 0·223 | 0·756 |
| 82·6 | 0·236 | 0 750 |
| 84·9 | 0·274 | 0·766 |

* For references see footnote at beginning of § 411.

verification is open to doubt, as the lowest temperatures are so high that further variations in $\Theta_D$ and failure of this $T^3$-law may well set in at lower temperatures.

**§ 415. Perfect mixed crystals.** So far we have considered only pure crystals made up of a single kind of molecule. We shall now extend the treatment to mixed crystals made up of several kinds of molecule in arbitrary proportions, but we shall confine ourselves here to the simple case where the different molecules are very much alike. The most important applications in view will be to mixtures of isotopes. We shall therefore assume that in the mixed crystal any pair of molecules of different kinds can be interchanged without appreciably affecting the volume, the configurational energy, or the frequencies of the normal modes of the crystal. Such mixed crystals are strictly analogous to the perfect mixed solutions discussed in Chapter VIII. We shall discuss particular cases where we make less restrictive assumptions in Chapter XIII.

Let us for the moment take as energy zero the lowest energy state of the crystal. Then we have already seen that the partition function for a pure crystal of $N$ molecules (or basal cells) can be put in the form $[\alpha(T)\,j(T)]^N$, where $\alpha(T)$ is the partition function per molecule for the acoustical modes, and $j(T)$ the partition function for the internal motions of each single molecule at its lattice point. Now let us suppose that we have a crystal made up of $N_A$ molecules of one kind and $N_B$ of another, arranged in some definite manner on $N_A+N_B$ lattice points. There is then first one distinct eigen function for the crystal in a state in which the oscillations in each molecule have given quantum numbers—one whether we ignore symmetry requirements or whether we make the crystal eigen function have the correct symmetry by permuting the $N_A$ molecules of type $A$ over their lattice points and the $N_B$ molecules of type $B$ over theirs. If we interchange an $A$ and a $B$, on the contrary, we obtain a significantly different crystal with very slightly different normal modes and energy levels. If mixing of the two sorts of molecule can occur, as we have assumed, in all positions without appreciable effect on the energy levels, there will be $(N_A+N_B)!/N_A!\,N_B!$ different crystals possible, each with very slightly different normal modes and energies. If we ignore these very small differences, there is the same partition function $[\alpha(T)]^{N_A+N_B}$ for the acoustical modes for each arrangement. The resulting partition function counting all the distinct arrangements will therefore be

$$\frac{(N_A+N_B)!}{N_A!\,N_B!}[\alpha(T)]^{N_A+N_B}. \qquad (415,1)$$

This formula has, however, allowed only for a single state of weight unity for the internal motions of each molecule. Those of the type $A$ will actually

provide a factor $j_A(T)$ for each $A$ molecule, and those of the type $B$ a factor $j_B(T)$. The complete partition function for the whole mixed crystal to this approximation will therefore be

$$K(T) = \frac{(N_A + N_B)!}{N_A!\,N_B!}[j_A(T)]^{N_A}[j_B(T)]^{N_B}[\alpha(T)]^{N_A+N_B}, \qquad (415, 2)$$

the energy zero being still the lowest energy state of the crystal. When, however, we use the more usual energy zero of the state of infinite dispersion, this becomes

$$K(T) = \frac{(N_A + N_B)!}{N_A!\,N_B!}[e^{\chi_A/kT}j_A(T)]^{N_A}[e^{\chi_B/kT}j_B(T)]^{N_B}[\alpha(T)]^{N_A+N_B}, \qquad (415, 3)$$

where $\chi_A$, $\chi_B$ are independent of the composition.

The usual thermodynamic functions can be obtained at once from

$$F = -kT \log K(T), \qquad (415, 4)$$

which continues to hold for any solid phase.

# CHAPTER V

## CHEMICAL EQUILIBRIA AND EVAPORATION. NERNST'S THEOREM

**§ 500. Introduction.** We now pass on to the general assembly, in which gaseous atoms and molecules react chemically, or evaporate from and condense on crystals. Generally speaking, we may say that we are now to investigate the equilibrium state of an assembly of practically independent systems, which no longer retain their individualities throughout the motion of the assembly, but are able to break up and recombine in such a way as to form any specified number of different types of independent systems. It will obviously be important to specify what we regard as the ultimate structural elements of the assembly—the indivisible systems which can combine, but never break up further. The formal exposition will be the same whatever the ultimate units are assumed to be, but the physical interpretation will be different. We shall for the sake of definiteness suppose that the ultimate units are the atoms of chemistry. Alternatively the same formulae can be reinterpreted in terms of positive nuclei and electrons in the study of the properties of matter at very high temperatures. This interpretation is obviously the more fundamental, and will of course include the former as a special case; in practice the two fields hardly overlap. In most assemblies hot enough to contain an appreciable equilibrium concentration of atomic ions and free electrons, the number of molecular species effectively present will be found to be negligible.

Previous to the accurate formulation of the quantum theory the most satisfactory discussion of the problems of dissociation, from the standpoint of pure statistical mechanics, was based on the work of Ehrenfest and Trkal.* These authors discuss the dissociation problem on semi-classical lines; they assume, that is, that all degrees of freedom of a system are either classical or unexcited. This restriction is here removed, so that the discussion is perfectly general, and subject only in its range of applicability to restrictions of a physical nature inherent in the problem. Thanks to the simplifications introduced by quantum theory, the method of analysis of Ehrenfest and Trkal need no longer be followed. Actual matter, however (for example, imperfect gases), will not always be comparable to an assembly analysed into practically independent systems. We shall make a first attempt in Chapters VII, VIII and IX towards the removal of this particular restriction.

* Ehrenfest and Trkal, *Proc. Sec. Sci. Amsterdam*, **23**, 162 (1920). We do not know of any earlier discussion of dissociation, or the kindred matters of "chemical constants", "thermodynamic probability", and "absolute entropy", which can be regarded as logically convincing.

**§ 501. Isomeric equilibrium.** Before deriving the general law of equilibrium, we shall consider some simple examples. We can obtain the special law for the simple case of *isomeric equilibrium* by elementary reasoning. We consider a system $A$, defined by its composition in terms of permanent particles, say atomic nuclei and electrons. Now suppose that its states can be divided into two sets having quantum numbers $r_1', r_2', \ldots$, and $r_1'', r_2'', \ldots$, respectively, such that the equilibrium distribution among the states $r_1', r_2', \ldots$, and the equilibrium distribution among the states $r_1'', r_2'', \ldots$, are each attained much more rapidly than is the equilibrium distribution between any of the $r'$ states and any of the $r''$ states. Then it may be possible to observe an assembly of such systems over an interval of time such that the two former distributions have reached equilibrium, whereas the last has not had time to adjust itself appreciably. In this case we attribute different names $A'$ and $A''$ to a system $A$, according as it is in one of the states $r'$ or one of the states $r''$. $A'$ and $A''$ are called isomers. We may assign separate partition functions $f'(T)$ and $f''(T)$ to the isomeric systems $A'$ and $A''$, defined by

$$f'(T) = \Sigma_{r'} \varpi_{r'} e^{-\epsilon_{r'}/kT}, \tag{501, 1}$$

$$f''(T) = \Sigma_{r''} \varpi_{r''} e^{-\epsilon_{r''}/kT}. \tag{501, 2}$$

Suppose now we wait a sufficient time for the distribution between the $A'$ and $A''$ to reach its average value, or alternatively that we speed up the transitions between $A'$ and $A''$ by means of a catalyst, and investigate what is the final average (complete equilibrium) distribution. In other words we study the equilibrium of the isomeric change

$$A' \rightleftarrows A''. \tag{501, 3}$$

When this complete equilibrium is reached, the average properties of the assembly are determined by the complete partition function,

$$f(T) = f'(T) + f''(T),$$

the two terms $f'(T)$ and $f''(T)$ referring to states in which the system is an $A'$ molecule and an $A''$ molecule respectively. Hence at complete equilibrium, the average numbers of $A'$ and $A''$ are given by

$$\overline{n_{A'}} : \overline{n_{A''}} : N = f'(T) : f''(T) : f(T). \tag{501, 4}$$

This is the simplest example of the law of mass action—for the equilibrium between two isomers.

As a matter of fact we have already assumed and made use of the equilibrium condition (4) in our discussion of para- and ortho-hydrogen. At low temperatures the properties of the two forms are separately determined by their two partition functions $f_p(T)$ and $f_o(T)$, but their relative proportions

can be varied independently. At high temperatures, or in presence of a catalyst, the equilibrium between the two forms is maintained, and this equilibrium is given according to (4) by

$$\overline{n_p}/\overline{n_o} = f_p(T)/f_o(T) = r_p(T)/3r_o(T), \tag{501, 5}$$

where $r_p(T)$ and $3r_o(T)$ are the rotational-nuclear partition functions of the two forms; the translational, vibrational and electronic partitions are the same for the two forms, and so cancel. At high temperatures the ratio $r_p(T)/3r_o(T)$ becomes $\frac{1}{3}$, and this is the ratio of the two forms in the metastable mixture obtained on cooling ordinary hydrogen in the absence of a catalyst.

§ **502. Simple dissociation.** We shall now give an elementary discussion of the simplest form of dissociative equilibrium, represented by the chemical formula

$$AB \rightleftarrows A + B. \tag{502, 1}$$

If each of the three species $AB$, $A$, $B$ behaves as a perfect gas, we may assign a partition function to each species. We denote these by $f_{AB}$, $f_A$, $f_B$ respectively. Suppose we now consider a definite pair of atoms $A$ and $B$. They can exist, either as a single molecule $AB$, or as a pair of free atoms. We can now assign a partition function $f_{(A+B)}$ to the pair regarded as one system. This will have the form

$$f_{(A+B)} = f_{AB} + f_A f_B, \tag{502, 2}$$

the first term referring to the molecular states $AB$ and the second term to the states of the free atoms $A$ and $B$. From this point of view of treating the pair of atoms as one system and making use of the distribution laws already derived in Chapter II, it is clear that the times spent by this particular pair of atoms in the molecular states and in the states of free atoms will be in the ratio $f_{AB} : f_A f_B$. If this is to be true simultaneously for all possible pairs of atoms, we must have the average distribution between molecules and free atoms given by

$$\overline{n_A}\,\overline{n_B}/\overline{n_{AB}} = f_A f_B/f_{AB}. \tag{502, 3}$$

This argument is plausible, but admittedly not logically convincing The result, however, can be rigorously established by an argument, which we shall outline briefly in the following section.

§ **503. Mathematical deduction.** We shall for the sake of brevity continue to consider the very simple equilibrium

$$AB \rightleftarrows A + B. \tag{503, 1}$$

The extension of the result to any more complicated equilibria will be obvious. Although we shall be interested only in classical statistics, the reasoning is equally simple for Fermi-Dirac or Bose-Einstein statistics, and

so we shall outline the argument for the general case. It is so simple and differs so little from that of §§ 214–217, that we need outline the reasoning only quite briefly.

Let the total number of atoms $A$, free or combined, be $N_A$, and the total number of atoms $B$, free or combined, be $N_B$. Since dissociation and recombination are assumed to proceed freely, the number of molecules $AB$ present in an accessible state of the assembly may have any value whatever from zero to $N_A$ or $N_B$ whichever is the less, and all such complexions have to be included in the enumeration. It is convenient to refer to all complexions, in which the number of free atoms $A$ has a specified value $n_A$, the number of free atoms $B$ has a specified value $n_B$, and the number of molecules $AB$ has a specified value $n_{AB}$, as an *example* of the assembly. We can sum the complexions for each example and then for all examples to obtain the total. For each example the values of $n_A$, $n_B$, $n_{AB}$ must satisfy the conditions

$$n_A + n_{AB} = N_A, \tag{503, 2}$$

$$n_B + n_{AB} = N_B. \tag{503, 3}$$

To find the number of complexions for a particular example $n_A$, $n_B$, $n_{AB}$, we can proceed exactly as in § 214 and construct the analogue of (214, 9), allowing for degenerate states, namely

$$\Pi_r(1 \pm xz^{\epsilon_r})^{\pm \varpi_r}\, \Pi_s(1 \pm yz^{\eta_s})^{\pm \varpi_s'}\, \Pi_t(1 \pm wz^{\zeta_t})^{\pm \varpi_t''}, \tag{503, 4}$$

where $\epsilon_r$, $\eta_s$, $\zeta_t$ are the energy values (referred to the same zeros), and $\varpi_r$, $\varpi_s'$ and $\varpi_t''$ weights, of the state $r$ of a free $A$ atom, the state $s$ of a free $B$ atom, and the state $t$ of an $AB$ molecule respectively. In each continued product the + or − sign is to be used according as the $A$ atoms, $B$ atoms, $AB$ molecules obey the Fermi-Dirac or the Bose-Einstein statistics; that is according as the $A$ atoms, the $B$ atoms, the $AB$ molecules contain an odd or even number of primary particles (electrons, protons, neutrons). The number of complexions of this example of the assembly with a total energy $E$ is then obtained as the coefficient of $x^{n_A} y^{n_B} w^{n_{AB}} z^E$ in (4).

It will be observed that, in accordance with the rules for enumeration laid down in § 108, we do not permute the free and bound atoms $A$ or the free and bound atoms $B$. Thus the coefficient of $x^{n_A} y^{n_B} w^{n_{AB}} z^E$ in (4) gives the total number of complexions of the assembly corresponding to the specification $n_A$ free $A$'s, $n_B$ free $B$'s and $n_{AB}$ molecules $AB$.

We have next to sum over all examples, that is over all sets of values of $n_A$, $n_B$, $n_{AB}$ satisfying (2) and (3). For this purpose we replace $w$ by $xy$, and use instead of (4) the expression

$$\Pi_r(1 \pm xz^{\epsilon_r})^{\pm \varpi_r}\, \Pi_s(1 \pm yz^{\eta_s})^{\pm \varpi_s'}\, \Pi_t(1 \pm xyz^{\zeta_t})^{\pm \varpi_t''}. \tag{503, 5}$$

The total number of complexions is then given by the coefficient of $x^{N_A} y^{N_B} z^E$

in (5), since this is equal to the sum of the coefficients of $x^{n_A} y^{n_B} w^{n_{AB}} z^E$ in (4) and all similar expressions, with values of $n_A$, $n_B$, $n_{AB}$ satisfying (2) and (3).

All average values are derived from (5) exactly as those for assemblies of permanent systems were derived in §§ 214–217, and the results can be written down immediately by analogy. The average number $\overline{n_r}$ of free atoms $A$ in the state $r$ of energy $\epsilon_r$ and weight $\varpi_r$ is given by

$$\overline{n_r} = \frac{\varpi_r \lambda_A \vartheta^{\epsilon_r}}{1 \pm \lambda_A \vartheta^{\epsilon_r}}, \tag{503, 6}$$

and similarly the average number $\overline{n_s}$ of free atoms $B$ in the state $s$ of energy $\eta_s$ and weight $\varpi'_s$ is given by

$$\overline{n_s} = \frac{\varpi'_s \lambda_B \vartheta^{\eta_s}}{1 \pm \lambda_B \vartheta^{\eta_s}}. \tag{503, 7}$$

The average number $\overline{n_t}$ of molecules $AB$ in the state $t$ of energy $\zeta_t$ and weight $\varpi''_t$ is given by

$$\overline{n_t} = \frac{\varpi''_t \lambda_A \lambda_B \vartheta^{\zeta_t}}{1 \pm \lambda_A \lambda_B \vartheta^{\zeta_t}}. \tag{503, 8}$$

All other average values can be derived from (6), (7) and (8). They can be summarized by the statement that the atoms $A$ and $B$ and the molecules $AB$ are each distributed over their states according to a formula of the type

$$\overline{n_r} = \frac{\varpi_r \lambda \vartheta^{\epsilon_r}}{1 \pm \lambda \vartheta^{\epsilon_r}}, \tag{503, 9}$$

where there is one $\vartheta$ for the whole assembly, but one $\lambda$ for the free atoms $A$, another for the free atoms $B$ and a third for the molecules $AB$. The three $\lambda$'s are not independent, but are related by the equation

$$\lambda_{AB} = \lambda_A \lambda_B. \tag{503, 10}$$

It follows at once from (6–8) that

$$\overline{n_A} = \Sigma_r \frac{\varpi_r \lambda_A \vartheta^{\epsilon_r}}{1 \pm \lambda_A \vartheta^{\epsilon_r}}, \quad \overline{n_B} = \Sigma_s \frac{\varpi'_s \lambda_B \vartheta^{\eta_s}}{1 \pm \lambda_B \vartheta^{\eta_s}}, \quad \overline{n_{AB}} = \Sigma_t \frac{\varpi''_t \lambda_{AB} \vartheta^{\zeta_t}}{1 \pm \lambda_{AB} \vartheta^{\zeta_t}}. \tag{503, 11}$$

The bars denoting average values will generally be omitted in future.

**§ 504. Relationship to thermodynamics.** As in § 223 we now define $F_A$, $F_B$, $F_{AB}$ by the equations

$$F_A \log \vartheta = \Sigma_r \varpi_r \log(1 \pm \lambda_A \vartheta^{\epsilon_r})^{\pm 1} - n_A \log \lambda_A, \tag{504, 1}$$

$$F_B \log \vartheta = \Sigma_s \varpi'_s \log(1 \pm \lambda_B \vartheta^{\eta_s})^{\pm 1} - n_B \log \lambda_B, \tag{504, 2}$$

$$F_{AB} \log \vartheta = \Sigma_t \varpi''_t \log(1 \pm \lambda_{AB} \vartheta^{\zeta_t})^{\pm 1} - n_{AB} \log \lambda_{AB}, \tag{504, 3}$$

each $\pm$ denoting $+$ for systems containing an odd number of primary

particles (electrons, protons, neutrons) and – for systems containing an even number. These functions are to be regarded as functions of $\vartheta$, $x$ (the geometrical coordinates), and $n_A$, $n_B$, $n_{AB}$; the apparent variables $\lambda_A$, ... being evaluated and substituted for in terms of $\vartheta$, $x$, $n_A$, ... by means of (503, 11). It is, however, inconvenient and unnecessary to carry out the actual substitution. We have only to observe that

$$\lambda_A \frac{\partial F_A}{\partial \lambda_A} = \Sigma_r \frac{\varpi_r \lambda_A \vartheta^{\epsilon_r}}{1 \pm \lambda_A \vartheta^{\epsilon_r}} - n_A = 0, \tag{504, 4}$$

and that similarly $\partial F_B/\partial \lambda_B = 0$ and $\partial F_{AB}/\partial \lambda_{AB} = 0$. We may therefore treat the $\lambda$'s in the $F$'s as quasi-constants, which need not be varied in any first order variation of $\vartheta$, $x$ or $n_A$, .... This is a feature of equilibrium formulae which we have already encountered, and shall frequently encounter again. We then define $F$ by

$$F = F_A + F_B + F_{AB}. \tag{504, 5}$$

We can then show exactly as in § 223 that the average value of the generalized force corresponding to the coordinate $x$ is given by

$$\bar{X} = -(\partial F/\partial x)_{\vartheta, n_A, n_B, n_{AB}}, \tag{504, 6}$$

and, exactly as in § 223, that the average energy $\bar{E}$ of the assembly is given by

$$\bar{E} = (\partial[F \log \vartheta]/\partial \log \vartheta)_{x, n_A, n_B, n_{AB}}. \tag{504, 7}$$

In deriving both formulae the $\lambda$'s need not be varied. We also find that

$$(\partial F/\partial n_A)_{\vartheta, x, n_B, n_{AB}} = -\log \lambda_A/\log \vartheta, \tag{504, 8}$$

$$(\partial F/\partial n_B)_{\vartheta, x, n_A, n_{AB}} = -\log \lambda_B/\log \vartheta, \tag{504, 9}$$

$$(\partial F/\partial n_{AB})_{\vartheta, x, n_A, n_B} = -\log \lambda_{AB}/\log \vartheta. \tag{504, 10}$$

We can now show that $F$ can be taken to be identical with the free energy of the assembly. If we define $T$, $\mu_A$, $\mu_B$, $\mu_{AB}$ by

$$-1/kT = \log \vartheta, \tag{504, 11}$$

$$\mu_A = -\log \lambda_A/\log \vartheta, \tag{504, 12}$$

$$\mu_B = -\log \lambda_B/\log \vartheta, \tag{504, 13}$$

$$\mu_{AB} = -\log \lambda_{AB}/\log \vartheta, \tag{504, 14}$$

then equations (6–10) become

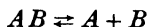
$$\bar{X} = -(\partial F/\partial x)_{T, n_A, n_B, n_{AB}}, \tag{504, 15}$$

$$\bar{E} = -T^2\left(\frac{\partial[F/T]}{\partial T}\right)_{x, n_A, n_B, n_{AB}}, \tag{504, 16}$$

$$(\partial F/\partial n_A)_{T, x, n_B, n_{AB}} = \mu_A, \tag{504, 17}$$

$$(\partial F/\partial n_B)_{T, x, n_A, n_{AB}} = \mu_B, \tag{504, 18}$$

$$(\partial F/\partial n_{AB})_{T, x, n_A, n} = \mu_{AB}. \tag{504, 19}$$

But these are the well-known formulae of thermodynamics, if $F$ is the free energy, $T$ the absolute temperature, and $\mu_A$, $\mu_B$, $\mu_{AB}$ the partial potentials of $A$, $B$, $AB$. We are entitled to interpret the symbols in this manner provided that the average distribution laws obtained by statistical mechanics agree with the laws of thermodynamics. The statistical theorem that there is a common $\vartheta$ value for the whole assembly agrees with the thermodynamic law that there is a common $T$ for the whole assembly. For the chemical equilibrium

$$AB \rightleftarrows A + B$$

we have deduced from statistical mechanics that the average distribution is determined by

$$\lambda_{AB} = \lambda_A \lambda_B. \qquad (504, 20)$$

Substituting from (12), (13), (14) this becomes

$$\mu_{AB} = \mu_A + \mu_B, \qquad (504, 21)$$

which is just Gibbs' thermodynamic condition for equilibrium, if we interpret the $\mu$'s as the partial potentials. We therefore obtain all the usual thermodynamic formulae and laws when we define the $F$ of (5) as the free energy, which justifies the interpretation.

It is to be particularly noted that this reasoning determines the dependence of the free energy $F$ and therefore also of the entropy $S$ on the $n$'s. This is because we have considered chemical reactions, in which the $n$'s were made to vary. A great part of the controversies about entropy in statistical mechanics has centred round the determination of the variation of the thermodynamic functions with the $n$'s, ignoring the fundamental point that such variations can only be relevant, and therefore determinable, when the $n$'s can change by a chemical or physico-chemical process. This has led to great confusion of thought,* only avoidable in some way equivalent to the foregoing.

**§ 505. Free energy and entropy of gaseous mixtures.** Now that the correlation between statistical and thermodynamic functions is completed, it is desirable to examine how the thermodynamic functions of a mixture of perfect gases are related to those of the single gases of which the mixture is composed. The absence of interaction between the molecules leads, as explained in § 301, to additivity of all the thermodynamic quantities $E$, $F$, $S$ when these are expressed as functions of $T$, $V$ and the $N$'s. This additivity of thermodynamic quantities can be expressed in the form

$$E = \Sigma_A N_A E_A^0(T), \qquad (505, 1)$$

$$F = \Sigma_A N_A\{F_A^0(T) + kT\log(N_A/V)\}, \qquad (505, 2)$$

$$S = \Sigma_A N_A\{S_A^0(T) - k\log(N_A/V)\}, \qquad (505, 3)$$

* For a critical exposition of this confusion, see Ehrenfest and Trkal, *Proc. Sec. Sci. Amsterdam*, **23**, 162 (1920).

where $E^0_A$, $F^0_A$, $S^0_A$ are functions of $T$ only, related to one another by

$$E^0_A - F^0_A = TS^0_A. \tag{505, 4}$$

In Chapter III we obtained detailed expressions for $E^0_A$, $F^0_A$, $S^0_A$, but what we now have to say is independent of these details.

The concentrations $N_A/V$, ... are related to the partial pressures $p_A$, ... by the formulae

$$p_A = kTN_A/V, \quad p_B = kTN_B/V, \; \dots. \tag{505, 5}$$

If we substitute from (5) into the above equalities, we notice that (1) is unaltered while (2) and (3) become

$$F = \Sigma_A N_A\{F^0_A(T) - kT\log kT + kT\log p_A\}, \tag{505, 6}$$

$$S = \Sigma_A N_A\{S^0_A(T) + k\log kT - k\log p_A\}, \tag{505, 7}$$

and we see that the additivity of $E$, $F$ and $S$ is preserved, when they are expressed as functions of the partial pressures instead of the concentrations.

It is sometimes convenient to take as independent variables the temperature, composition and *total pressure*. To obtain the relevant formulae we have to use the equation

$$P = \Sigma_A N_A kT/V. \tag{505, 8}$$

Substituting for $V$ in (2) and (3) we now obtain

$$F = \Sigma_A N_A\{F^0_A(T) - kT\log kT + kT\log P\} + \Sigma_A N_A kT\log\frac{N_A}{N_A + N_B + \dots}, \tag{505, 9}$$

$$S = \Sigma_A N_A\{S^0_A(T) + k\log kT - k\log P\} + \Sigma_A N_A k\log\frac{N_A + N_B + \dots}{N_A}. \tag{505, 10}$$

We thus see that the free energy of the mixture exceeds the free energy of the component gases at the same temperature and at the same *total pressure* as the mixture by the (negative) quantity $\Delta F$ given by

$$\Delta F = \Sigma_A N_A kT\log\frac{N_A}{N_A + N_B + \dots}. \tag{505, 11}$$

Similarly the entropy of the mixture exceeds the entropy of the component gases at the same temperature and at the same *total pressure* as the mixture by the (positive) quantity $\Delta S$ given by

$$\Delta S = \Sigma_A N_A k\log\frac{N_A + N_B + \dots}{N_A}. \tag{505, 12}$$

The quantity $\Delta S$ is often referred to by the name *entropy of mixing*; the analogous name for $\Delta F$ is the *free energy of mixing*. The nomenclature is well established, but can be confusing, if it is not remembered that the total pressure must be chosen as one of the independent variables. When the

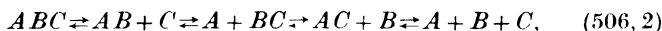
partial pressures or the total volume are chosen as independent variables, instead of the total pressure, we have seen that there is complete additivity of both free energy and entropy.

**§ 506. General chemical equilibrium.** The extension of these results to the most general type of chemical equilibrium is immediate. For each chemical species, such as for example $AB$, which has states $r$ of energy $\epsilon_r$ and weight $\varpi_r$, the equilibrium distribution amongst the states is given by

$$n_r = \frac{\varpi_r \lambda_{AB} e^{-\epsilon_r/kT}}{1 \pm \lambda_{AB} e^{-\epsilon_r/kT}}, \tag{506, 1}$$

where $T$ is the absolute temperature, the $+$ or $-$ is determined by the nature of $AB$, and the absolute activity $\lambda_{AB}$ has the same value for all the states of the molecule $AB$.

The absolute activities $\lambda$ for the different species are, as we have seen, not independent. Corresponding to all possible chemical changes such as

$$ABC \rightleftarrows AB + C \rightleftarrows A + BC \rightleftarrows AC + B \rightleftarrows A + B + C, \tag{506, 2}$$

we have relations of the form

$$\lambda_{ABC} = \lambda_{AB}\lambda_C = \lambda_A \lambda_{BC} = \lambda_{AC}\lambda_B = \lambda_A \lambda_B \lambda_C. \tag{506, 3}$$

These relations reduce the number of independent absolute activities $\lambda$ to the number of atomic species $A$, $B$, $C$, ....

Finally the values of the absolute activities $\lambda$ are determined by the necessary equalities such as

$$n_A + n_{AB} + n_{AC} + \ldots + 2n_{AA} + \ldots + n_{ABC} + n_{ABD} + n_{ACD} + \ldots$$
$$+ 2n_{AAB} + \ldots + n_{ABCD} + \ldots + \ldots = N_A, \tag{506, 4}$$

where $N_A$ is the total number of atoms $A$, free or combined, in the assembly. There is one relation of this type for each atomic species, and so just sufficient relations to determine all the absolute activities, and so all the average (equilibrium) properties of the assembly.

These formulae for average properties simplify considerably when we may use classical statistics, that is when the $\lambda$'s are sufficiently small, as is in practice always the case. For each chemical species such as, for example, $AB$, which has states $r$ of energy $\epsilon_r$ and weight $\varpi_r$, the distribution law (1) simplifies to

$$n_r = \lambda_{AB} \varpi_r e^{-\epsilon_r/kT}, \tag{506, 5}$$

the $\lambda$'s for the various molecular species being related by formulae of the type (3).

If we sum (5) over all states of the molecular species $AB$, we obtain

$$n_{AB} = \lambda_{AB} f_{AB}(T), \tag{506, 6}$$

where $f_{AB}(T)$ is the partition function of the systems $AB$. From (6) we see that in a gas of given temperature and volume the absolute activity of each species is directly proportional to the number of molecules of that species. We can use (3) to eliminate the $\lambda$'s between (6) and similar formulae. We obtain relations such as

$$\frac{n_{ABC}}{f_{ABC}} = \frac{n_{AB}n_C}{f_{AB}f_C} = \frac{n_A n_{BC}}{f_A f_{BC}} = \frac{n_{AC}n_B}{f_{AC}f_B} = \frac{n_A n_B n_C}{f_A f_B f_C}. \qquad (506, 7)$$

Now each partition function $f$ can be factorized into a translational partition function $l$, and an internal partition function $j$. The former is directly proportional to $V$ and the latter independent of $V$. It is clear then that the classical law of mass action is included in (7).

§ 507. **Shift of energy zero.** For the validity of formulae such as (506, 7) it is essential that all inter-connected energy levels should be referred to the same zero, such as the state of complete dissociation into free atoms in their lowest quantum states. As far as atomic states are concerned this is the obvious choice, but for molecular states it is sometimes more convenient to use as zero the lowest quantum state of the isolated molecule. If we wish to use this, or any other energy zero, for the molecules, disagreeing with the energy zero for the atoms, we must modify formulae such as (506, 7) as follows:

$$\frac{n_{ABC}}{f_{ABC}e^{-\epsilon^0_{ABC}/kT}} = \frac{n_{AB}n_C}{f_{AB}e^{-\epsilon^0_{AB}/kT}f_C} = \frac{n_A n_{BC}}{f_A f_{BC}e^{-\epsilon^0_{BC}/kT}}$$

$$= \frac{n_{AC}n_B}{f_{AC}e^{-\epsilon^0_{AC}/kT}f_B} = \frac{n_A n_B n_C}{f_A f_B f_C}, \qquad (507, 1)$$

where $\epsilon^0_{ABC}$, $\epsilon^0_{AB}$, $\epsilon^0_{BC}$, $\epsilon^0_{AC}$ are the excess energies of the states chosen for zeros in the molecular partition functions over the atomic energy zeros. The $\epsilon^0$'s will usually have negative values.

§ 508. **Detailed formulae for dissociation of diatomic molecules.** Let us now consider in more detail the formulae for the dissociative equilibrium of a diatomic molecule, say

$$AB \rightleftarrows A + B. \qquad (508, 1)$$

The atomic partition functions are given by

$$f_A = \frac{(2\pi m_A kT)^{\frac{3}{2}}}{h^3} V v_{0A} \rho_A, \qquad (508, 2)$$

$$f_B = \frac{(2\pi m_B kT)^{\frac{3}{2}}}{h^3} V v_{0B} \rho_B, \qquad (508, 3)$$

where $m_A$, $m_B$ are the masses of the atoms; $\upsilon_{0A}$, $\upsilon_{0B}$ are the electronic weights of their normal states; $\rho_A$, $\rho_B$ are the nuclear spin weights. The molecular partition function is given to a sufficient approximation by the factorized form

$$f_{AB} = \frac{\{2\pi(m_A + m_B)kT\}^{\frac{3}{2}}}{h^3} Vr(T)q(T)\upsilon_{0AB}\frac{\rho_A\rho_B}{\sigma_{AB}}, \qquad (508, 4)$$

where $r(T)$ is the rotational partition function defined according to (315, 7); $q(T)$ is the vibrational partition function; $\upsilon_{0AB}$ is the weight of the lowest electronic state; $\rho_A$, $\rho_B$ are the nuclear spin weights, and $\sigma_{AB}$ is the symmetry number, equal to 2 if $A$ and $B$ are identical atoms, and to 1 otherwise. The energy zero is the lowest quantum state of the molecule $AB$. Using these values for the partition functions, the equilibrium state of the assembly is given by

$$\frac{n_A n_B}{n_{AB}} = \frac{f_A f_B}{f_{AB}} e^{\epsilon^0_{AB}/kT}$$

$$= V\frac{(2\pi m_A m_B kT)^{\frac{3}{2}}}{(m_A + m_B)^{\frac{3}{2}} h^3}\frac{e^{\epsilon^0_{AB}/kT}}{r(T)q(T)}\frac{\sigma_{AB}\upsilon_{0A}\upsilon_{0B}}{\upsilon_{0AB}}, \qquad (508, 5)$$

where $\epsilon^0_{AB}$ is defined in § 507, and is usually negative.

We notice that in (5) the nuclear spin weights for the molecule have just cancelled those for the atoms. It is obvious that this must happen if the atoms $A$ and $B$ are of different kinds. It also happens if the atoms $A$ and $B$ are identical, whenever the rotational-nuclear partition function $r_n(T)$ may be factorized as

$$r_n(T) = r(T)\rho_A\rho_B/\sigma_{AB}. \qquad (508, 6)$$

The condition for this is that the rotational degrees of freedom should be classical or nearly classical. For the accurate formula for $r_n(T)$ for a symmetrical molecule $AA$ is

$$r_n(T) = \tfrac{1}{2}\rho(\rho - 1)r_p(T) + \tfrac{1}{2}\rho(\rho + 1)r_o(T), \qquad (508, 7)$$

where $r_p(T)$ and $r_o(T)$ are the sums of alternate terms in the rotational partition function $r(T)$. One of these contains all the even terms, the other all the odd terms. Which is which depends on whether the nuclei have an odd or even mass. If now the rotational degrees of freedom are classical or nearly classical, we have with a high degree of accuracy

$$r_p(T) = r_o(T) = \tfrac{1}{2}r(T), \qquad (508, 8)$$

and so (7) reduces to

$$r_n(T) = \tfrac{1}{2}r(T)\rho^2, \qquad (508, 9)$$

in agreement with (6). We shall see in § 510 that a similar rule holds for polyatomic molecules.

In terms of the concentrations $c_A$, $c_B$, $c_{AB}$ defined by

$$c_A = n_A/V, \quad c_B = n_B/V, \quad c_{AB} = n_{AB}/V, \qquad (508, 10)$$

equation (5) becomes

$$\frac{c_A c_B}{c_{AB}} = \frac{(2\pi m_A m_B kT)^{\frac{3}{2}}}{(m_A+m_B)^{\frac{3}{2}} h^3} \frac{\sigma_{AB} v_{0A} v_{0B}}{r(T)\, q(T)\, v_{0AB}} e^{\epsilon^0_{AB}/kT}. \tag{508, 11}$$

In all practical applications to dissociative equilibrium $r(T)$ may with sufficient accuracy be assumed to have its classical value (314, 1), and (11) then becomes

$$\frac{c_A c_B}{c_{AB}} = \frac{(2\pi m_A m_B kT)^{\frac{3}{2}}}{(m_A+m_B)^{\frac{3}{2}} h^3} \frac{h^2}{8\pi^2 A kT} \frac{\sigma_{AB} v_{0A} v_{0B}}{q(T)\, v_{0AB}} e^{\epsilon^0_{AB}/kT}, \tag{508, 12}$$

where $A$ is the moment of inertia of the molecule $AB$. This can alternatively be expressed in terms of partial vapour pressures in the form

$$\frac{p_A p_B}{p_{AB}} = \frac{(2\pi m_A m_B)^{\frac{3}{2}} (kT)^{\frac{5}{2}}}{(m_A+m_B)^{\frac{3}{2}} h^3} \frac{h^2}{8\pi^2 A kT} \frac{\sigma_{AB} v_{0A} v_{0B}}{q(T)\, v_{0AB}} e^{\epsilon^0_{AB}/kT}. \tag{508, 13}$$

The form of $q(T)$ depends on the temperature range, and is discussed in § 320.

**§ 509. Isotopic diatomic molecules.** Another interesting simple example of the general chemical equilibrium is a gaseous mixture of isotopic diatomic molecules. For the sake of definiteness we shall consider the equilibrium between hydrogen and deuterium,

$$H_2 + D_2 \rightleftarrows 2HD, \tag{509, 1}$$

but the formulae obtained will be applicable to any similar equilibrium between isotopic diatomic molecules. The equilibrium is given in our usual notation by

$$\frac{n^2_{HD}}{n_{H_2} n_{D_2}} = \frac{f^2_{HD}}{f_{H_2} f_{D_2}}$$
$$= \frac{l^2_{HD}}{l_{H_2} l_{D_2}} \frac{r^2_{HD}}{r_{H_2} r_{D_2}} \frac{q^2_{HD}}{q_{H_2} q_{D_2}} \frac{v^2_{0HD}}{v_{0H_2} v_{0D_2}} \frac{\sigma^2_{HD}}{\sigma_{H_2}\sigma_{D_2}} \frac{(\rho_H \rho_D)^2}{\rho^2_H \rho^2_D} e^{-(2\epsilon^0_{HD} - \epsilon^0_{H_2} - \epsilon^0_{D_2})/kT}. \tag{509, 2}$$

Let us now examine how the isotopic differences enter into the separate factors of (2), assuming that the rotations as well as the translations are classical.

(1) The nuclear orientational factor $(\rho_H \rho_D)^2/\rho^2_H \rho^2_D$ in (2) is identically unity.

(2) The translational partition functions of the three molecular species differ from one another only through the differences of mass. Hence the translational factor in (2) becomes

$$\frac{l^2_{HD}}{l_{H_2} l_{D_2}} = \frac{(m_H + m_D)^3}{(2m_H)^{\frac{3}{2}} (2m_D)^{\frac{3}{2}}} = \left(\frac{m_H + m_D}{2 m_H^{\frac{1}{2}} m_D^{\frac{1}{2}}}\right)^3. \tag{509, 3}$$

(3) The rotational partition functions of the three species differ from one another only through the differences of moment of inertia. The rotational factor in (2) is therefore

$$\frac{r_{\mathrm{HD}}^2}{r_{\mathrm{H_2}}r_{\mathrm{D_2}}} = \frac{A_{\mathrm{HD}}^2}{A_{\mathrm{H_2}}A_{\mathrm{D_2}}}, \tag{509, 4}$$

where the $A$'s denote moments of inertia.

(4) The form of the vibrational partition functions will depend on the temperature. Usually at ordinary temperatures we have in each molecular species $h\nu \gg kT$, and so each $q(T)$, and therefore the complete factor, becomes unity. In the opposite extreme of temperatures so high that $kT \gg h\nu$, we have for $q(T)$ the limiting form $kT/h\nu$, which for the three molecular species will differ through the factor $\nu$. Thus we have the two limiting cases

$$\frac{q_{\mathrm{HD}}^2}{q_{\mathrm{H_2}}q_{\mathrm{D_2}}} = 1 \quad (kT \ll h\nu), \tag{509, 5}$$

$$\frac{q_{\mathrm{HD}}^2}{q_{\mathrm{H_2}}q_{\mathrm{D_2}}} = \frac{\nu_{\mathrm{H_2}}\nu_{\mathrm{D_2}}}{\nu_{\mathrm{HD}}^2} \quad (kT \gg h\nu). \tag{509, 6}$$

(5) The electronic states are identical for all three molecular species and the resultant factor is unity.

(6) The symmetry numbers are 2 for $H_2$ and $D_2$, but 1 for HD. The resultant factor in (2) is therefore 4.

Collecting these results we see that (2) becomes

$$\frac{n_{\mathrm{HD}}^2}{n_{\mathrm{H_2}}n_{\mathrm{D_2}}} = 4\left(\frac{m_{\mathrm{H}}+m_{\mathrm{D}}}{2m_{\mathrm{H}}^{\frac{1}{2}}m_{\mathrm{D}}^{\frac{1}{2}}}\right)^3 \frac{A_{\mathrm{HD}}^2}{A_{\mathrm{H_2}}A_{\mathrm{D_2}}} e^{-(2\epsilon^0_{\mathrm{HD}}-\epsilon^0_{\mathrm{H_2}}-\epsilon^0_{\mathrm{D_2}})/kT} \quad (kT \ll h\nu), \tag{509, 7}$$

$$\frac{n_{\mathrm{HD}}^2}{n_{\mathrm{H_2}}n_{\mathrm{D_2}}} = 4\left(\frac{m_{\mathrm{H}}+m_{\mathrm{D}}}{2m_{\mathrm{H}}^{\frac{1}{2}}m_{\mathrm{D}}^{\frac{1}{2}}}\right)^3 \frac{A_{\mathrm{HD}}^2}{A_{\mathrm{H_2}}A_{\mathrm{D_2}}} \frac{\nu_{\mathrm{H_2}}\nu_{\mathrm{D_2}}}{\nu_{\mathrm{HD}}^2} e^{-(2\epsilon^0_{\mathrm{HD}}-\epsilon^0_{\mathrm{H_2}}-\epsilon^0_{\mathrm{D_2}})/kT} \quad (kT \gg h\nu). \tag{509, 8}$$

It may safely be assumed that the internuclear forces and distances in these molecules are practically unaffected by change of mass. This being so,

$$A_{\mathrm{H_2}} : A_{\mathrm{D_2}} : A_{\mathrm{HD}} = m_{\mathrm{H}} : m_{\mathrm{D}} : 2m_{\mathrm{H}}m_{\mathrm{D}}/(m_{\mathrm{H}}+m_{\mathrm{D}}), \tag{509, 9}$$

$$\nu_{\mathrm{H_2}} : \nu_{\mathrm{D_2}} : \nu_{\mathrm{HD}} = m_{\mathrm{H}}^{-\frac{1}{2}} : m_{\mathrm{D}}^{-\frac{1}{2}} : \{2m_{\mathrm{H}}m_{\mathrm{D}}/(m_{\mathrm{H}}+m_{\mathrm{D}})\}^{-\frac{1}{2}}. \tag{509, 10}$$

Further the $\epsilon^0$'s will differ only by the residual energy of the lowest vibrational levels, so that

$$2\epsilon^0_{\mathrm{HD}} - \epsilon^0_{\mathrm{H_2}} - \epsilon^0_{\mathrm{D_2}} = \tfrac{1}{2}h(2\nu_{\mathrm{HD}} - \nu_{\mathrm{H_2}} - \nu_{\mathrm{D_2}}) = h\nu_{\mathrm{HD}}\left\{1 - \frac{\frac{1}{2}(m_{\mathrm{H}}^{\frac{1}{2}} + m_{\mathrm{D}}^{\frac{1}{2}})}{(\frac{1}{2}m_{\mathrm{H}} + \frac{1}{2}m_{\mathrm{D}})^{\frac{1}{2}}}\right\}. \tag{509, 11}$$

Equations (7) and (8) then reduce to

$$\frac{n_{\mathrm{HD}}^2}{n_{\mathrm{H}_2} n_{\mathrm{D}_2}} = 4\left(\frac{m_{\mathrm{H}} + m_{\mathrm{D}}}{2m_{\mathrm{H}}^{\frac{1}{2}} m_{\mathrm{D}}^{\frac{1}{2}}}\right) \exp\left\{-\frac{h\nu_{\mathrm{HD}}}{kT}\left[1 - \frac{\frac{1}{2}(m_{\mathrm{H}}^{\frac{1}{2}} + m_{\mathrm{D}}^{\frac{1}{2}})}{(\frac{1}{2}m_{\mathrm{H}} + \frac{1}{2}m_{\mathrm{D}})^{\frac{1}{2}}}\right]\right\} \quad (kT \ll h\nu), \tag{509, 12}$$

$$\frac{n_{\mathrm{HD}}^2}{n_{\mathrm{H}_2} n_{\mathrm{D}_2}} = 4 \exp\left\{-\frac{h\nu_{\mathrm{HD}}}{kT}\left[1 - \frac{\frac{1}{2}(m_{\mathrm{H}}^{\frac{1}{2}} + m_{\mathrm{D}}^{\frac{1}{2}})}{(\frac{1}{2}m_{\mathrm{H}} + \frac{1}{2}m_{\mathrm{D}})^{\frac{1}{2}}}\right]\right\} \quad (kT \gg h\nu). \tag{509, 13}$$

Equation (12) applies to hydrogen and deuterium at experimental temperatures. Inserting numerical values ($\nu_{\mathrm{HD}} = 3770$ cm.$^{-1}$), we find an equilibrium constant given by

$$K = \frac{n_{\mathrm{HD}}^2}{n_{\mathrm{H}_2} n_{\mathrm{D}_2}} = 4 \times 1{\cdot}06\, e^{-78/T}. \tag{509, 14}$$

A comparison of values so calculated with the experimental values is given in Table 1. The agreement is excellent. It should be mentioned that at the lowest temperature, 195° K., the rotations can no longer be regarded as classical, and so our formulae are no longer strictly applicable. A more exact calculation* leads to the value $K = 2{\cdot}87$ at 195° K.

TABLE 1

*Values of equilibrium constant* $K = n_{\mathrm{HD}}^2/n_{\mathrm{H}_2} n_{\mathrm{D}_2}$.
*Values calculated from* $K = 4 \times 1{\cdot}06\ e^{-78/T}$

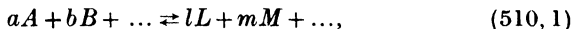
| Temperature ° K. | 195 | 273 | 298 | 383 | 543 | 670 | 741 |
|---|---|---|---|---|---|---|---|
| $K$ experimental | 2·92 | 3·24 | 3·28 | 3·50 | 3·85 | 3·8 | 3·70 |
| R.M.S. deviations | ± 0·08 | ± 0·08 | — | ± 0·06 | ± 0·10 | ± 0·4 | ± 0·12 |
| $K$ calculated | (2·84) | 3·18 | 3·26 | 3·46 | 3·67 | 3·77 | 3·81 |

Experimental values from Rittenberg, Bleakney and Urey, *J. Chem. Phys.* **2**, 48 (1934); Gould, Bleakney and Taylor, *J. Chem. Phys.* **2**, 362 (1934).

The equilibrium, here discussed,† between hydrogen and deuterium is an extreme case. For the isotopes of chlorine, of masses 35 and 37, either (7) or (8) leads to $K = 4(1-\delta)$, with $\delta \simeq 10^{-4}$, which is negligible.

## § 510. Chemical constants.

It is convenient at this stage to translate the general laws of homogeneous gaseous chemical equilibria into a more familiar thermodynamic form. We consider the general gaseous reaction

$$aA + bB + \ldots \rightleftarrows lL + mM + \ldots, \tag{510, 1}$$

where $A, B, \ldots, L, M, \ldots$ denote molecular species and $a, b, \ldots, l, m, \ldots$ are

* Urey and Rittenberg, *J. Chem. Phys.* **1**, 137 (1933). These authors have calculated $K$ to four significant figures for the temperature range 50–700° K. Deviations between these values and those given by formula (14) become appreciable only below 300° K.

† Details of the analogous calculation for equilibria between triatomic isotopic molecules are given by Jones and Sherman, *J. Chem. Phys.* **5**, 375 (1937).

small positive integers. We can abbreviate (1) to

$$\Sigma aA \rightleftarrows \Sigma lL. \tag{510, 2}$$

The condition for chemical equilibrium is

$$\Sigma a\mu_A = \Sigma l\mu_L. \tag{510, 3}$$

Now we have for each partial potential $\mu$ a formula of a definite type, according to whether the species is monatomic, diatomic, polyatomic linear or non-linear. We have already obtained these formulae in Chapter III on the assumption that the rotational degrees of freedom are classical. They were there expressed as functions of the concentrations $N/V$, and alternatively as functions of the partial pressures $p$. The two forms are of course simply correlated by use of the equation of state in the form

$$p_A = \frac{N_A}{V} kT. \tag{510, 4}$$

For our present purpose it is convenient to regard $\mu_A$ as a function of the partial pressure $p_A$. In Chapter III we chose as the internal energy zero for each molecular species the state of lowest internal energy. This choice is the natural one as long as each molecular species is regarded as a permanent system. But we are now allowing molecules to react with one another chemically, and it is therefore necessary to revise the energy zeros, so that they become consistent with the energy changes accompanying chemical reaction. We therefore denote the energy of the lowest internal state of the molecule $A$ by $\epsilon_A^0$. We may, if we wish, set $\epsilon_A^0$ zero for the usual molecular form of each element, but $\epsilon_A^0$ will still differ from zero for compounds. The partial potential $\mu_A$ will now contain an extra term $\epsilon_A^0$ as compared with the formulae used in Chapter III. For convenience we collect the several formulae here.

*Monatomic molecules*: compare (316, 3)

$$\log\lambda = \frac{\mu}{kT} = \frac{\epsilon^0}{kT} + \log p - \tfrac{5}{2}\log T - \log\left\{\frac{(2\pi m)^{\frac{3}{2}}k^{\frac{5}{2}}}{h^3} v_0 \rho\right\}. \tag{510, 5}$$

*Diatomic molecules*: compare (321, 3)

$$\log\lambda = \frac{\mu}{kT} = \frac{\epsilon^0}{kT} + \log p - \tfrac{7}{2}\log T - \log q(T) - \log\left\{\frac{(2\pi m)^{\frac{3}{2}}k^{\frac{5}{2}}}{h^3}\frac{8\pi^2 Ak}{h^2} v_0 \frac{\rho_A\rho_B}{\sigma}\right\}. \tag{510, 6}$$

*Polyatomic linear molecules*: compare (329, 7)

$$\log\lambda = \frac{\mu}{kT} = \frac{\epsilon^0}{kT} + \log p - \tfrac{7}{2}\log T - \Sigma_r \log q_r(T) - \log\left\{\frac{(2\pi m)^{\frac{3}{2}}k^{\frac{5}{2}}}{h^3}\frac{8\pi^2 Ak}{h^2} v_0 \frac{\Pi\rho}{\sigma}\right\}. \tag{510, 7}$$

*Non-linear molecules*: compare (329, 8)

$$\log\lambda = \frac{\mu}{kT} = \frac{\epsilon^0}{kT} + \log p - 4\log T - \Sigma_v \log q_v(T)$$
$$-\log\left\{\frac{(2\pi m)^{\frac{3}{2}}k^{\frac{5}{2}}}{h^3}\frac{8\pi^2(2\pi k)^{\frac{3}{2}}(ABC)^{\frac{1}{2}}}{h^3}v_0\frac{\Pi\rho}{\sigma}\right\}. \quad (510, 8)$$

In these formulae $m$ is the molecular mass, $A$, $B$, $C$ are principal moments of inertia, $q(T)$ or $q_v(T)$ is the partition function for a single vibration, $v_0$ is the electronic weight of the normal state, $\sigma$ is the symmetry number, and $\Pi\rho$ is the product of the nuclear spin weights.

All these formulae for different types of molecules are conveniently summarized in the form

$$\log\lambda = \frac{\mu}{kT} = \frac{\epsilon^0}{kT} + \log p - \frac{C_P^0}{k}\log T - \Sigma_v \log q_v(T) - j - \Sigma\log\rho, \quad (510, 9)$$

where $C_P^0$, $j$ are molecular constants (independent of $T$, $p$). Their values are as follows:

*Monatomic molecules*: $[q_v(T) = 1]$

$$C_P^0/k = \tfrac{5}{2}, \quad j = \log\left\{\frac{(2\pi m)^{\frac{3}{2}}k^{\frac{5}{2}}}{h^3}v_0\right\}. \quad (510, 10)$$

*Diatomic molecules and polyatomic linear molecules*:

$$C_P^0/k = \tfrac{7}{2}, \quad j = \log\left\{\frac{(2\pi m)^{\frac{3}{2}}k^{\frac{5}{2}}}{h^3}\frac{8\pi^2 Ak}{h^2}\frac{v_0}{\sigma}\right\}. \quad (510, 11)$$

*Non-linear molecules*

$$C_P^0/k = 4, \quad j = \log\left\{\frac{(2\pi m)^{\frac{3}{2}}k^{\frac{5}{2}}}{h^3}\frac{8\pi^2(2\pi k)^{\frac{3}{2}}(ABC)^{\frac{1}{2}}}{h^2}\frac{v_0}{\sigma}\right\}. \quad (510, 12)$$

We can now compare these statistical formulae with formulae obtained entirely by classical thermodynamics. We shall assume that for each gas there is a range of temperature in which the rotational degrees of freedom are classical (unless the molecule is monatomic), while the vibrational degrees of freedom are unexcited. We select any temperature in this range and denote it by $T^0$. We now write formally

$$C'(T) = C_P - C_P^0 \quad (T > T^0),$$
$$C'(T) = 0 \quad (T < T^0), \quad (510, 13)$$

where $C_P^0$ is the constant value of $C_P$ in the temperature range around $T^0$, while $C'(T)$ represents deviations of $C_P$ from this value at higher temperatures. Thus $C'(T) \to 0$ as $T \to T^0$. It is evident that $C_P^0$ thus defined is

the same quantity as that hitherto denoted by the same symbol. We can then by pure thermodynamics derive* for $\mu$ the formula

$$\frac{\mu}{kT} = \frac{H^0}{kT} + \log p - \frac{C_P^0}{k}\log T - \int_0^T \frac{dT_1}{T_1^2}\int_0^{T_1} \frac{C'(T_2)}{k}\,dT_2 - j_0, \quad (510, 14)$$

where $H^0$ is the value to which $H$ tends as $T \to 0$ and $j_0$ is a molecular constant independent of $T$ and $p$. The value of this integration constant $j_0$ is left undetermined by thermodynamics, but we shall see that it is determined by the statistical formulae which have already been obtained.

Let us compare the thermodynamic formula (14) with the statistical formula (9). Since for a perfect gas $H = E + kT$, it follows that for $T = 0$ there is no difference between $H$ and $E$ so that $H^0 = E^0 = \epsilon^0$. Thus the terms in the two formulae proportional to $1/T$ agree. The terms containing $p$ and $C_P^0$ evidently also agree. We can also show that the term containing $C'(T)$ in (14) is equal to $-\Sigma_v \log\{q_v(T)/q_v(0)\}$, when $q_v(T)$ is so defined that the energy of the lowest state is zero: $q_v(0)$ is the weight of the lowest vibrational state for the normal mode $v$, and this weight is always unity. Hence the term containing $C'(T)$ in (14) is equal to the term $-\Sigma_v \log q_v(T)$ in (9).

The integration constant $j_0$ in (14) is represented by $j + \Sigma \log \rho$ in (9). There is thus complete agreement between the statistical formula (9) and the thermodynamic formula (14). But the statistical method leads to an evaluation of the integration constant $j_0$ about which the thermodynamic method gives no information. The constants $j$ are called the chemical constants of the relevant molecules.

The reason for separating the term $\Sigma \log \rho$ in (9) instead of including it in $j$ is that, in applying (9) to any chemical equilibrium, we shall find that all the terms involving nuclear spin weights cancel, and there is therefore no need to evaluate them. The term $\Sigma \log \rho$ is thus chemically unimportant, and could be omitted without affecting any chemical deductions. It is not even necessary to know the nuclear spin weights, and actually they are not yet all known. This cancellation of the nuclear spin weights is dependent on the rotational degrees of freedom of the gaseous molecules being at least approximately classical. For strictly the rotational-nuclear partition function is the sum of terms each of which is the product of a nuclear spin weight and a rotational factor. These terms can be grouped according to the symmetry properties of the rotational eigen functions, and the nuclear spin weight factor will have the same value for each of these groups, but will vary from one group to another. A rotational-nuclear partition function of this form cannot strictly be factorized into a rotational and a nuclear factor. But if the rotational degrees of freedom are classical or nearly classical, then

* See *M.T.* Chapter XIV.

it can be shown that, with a high degree of accuracy (except for $H_2$, $D_2$ at low temperatures),

$$r_n(T) = r(T)\frac{\Pi\rho}{\sigma}, \tag{510, 15}$$

where $r(T)$ is the complete rotational partition function containing terms for all rotational states whatever their symmetry properties, $\Pi\rho$ is the product of the nuclear spin weights of the atoms present in the molecule, and $\sigma$ is the symmetry number of the molecule, defined as the number of indistinguishable orientations of the molecule. Fortunately the approximation (15) is adequate in all chemical applications, and we shall see that consequently all nuclear spin weights may be ignored.

Let us now transform the equilibrium condition (3) for the chemical reaction (1) or (2) into the familiar law of mass action in terms of partial vapour pressures, namely

$$\frac{\Pi_L(p_L)^l}{\Pi_A(p_A)^a} = K_p(T). \tag{510, 16}$$

By using (9) for the partial potential of each species, we find that

$$\log K_p = -\frac{1}{kT}\{\Sigma_L l\epsilon_L^0 - \Sigma_A a\epsilon_A^0\} + \left\{\Sigma_L l\frac{(C_P^0)_L}{k} - \Sigma_A a\frac{(C_P^0)_A}{k}\right\}\log T$$
$$+\{\Sigma_L l\Sigma_v \log q_{v,L}(T) - \Sigma_A a\Sigma_v \log q_{v,A}(T)\} + \{\Sigma_L lj_L - \Sigma_A aj_A\}. \tag{510, 17}$$

The values of $C_P^0/k$ and $j$ are given by (10), (11), (12) for monatomic, linear, and non-linear molecules respectively. It is now evident that the nuclear weights cancel. Formula (17) can also be written as

$$\log K_p = -\frac{\Delta H^0}{kT} + \frac{\Delta\Sigma C_P^0}{k}\log T + \int_0^T \frac{dT_1}{T_1^2}\int_0^{T_1}\frac{\Delta\Sigma C'(T_2)}{k}dT_2 + \Delta\Sigma j, \tag{510, 18}$$

where the operator $\Delta$ denotes the increase in the value of any quantity when the chemical reaction takes place to the extent represented by $\Sigma aA \to \Sigma lL$. $\Delta H^0$ is the limiting value of $\Delta H$ or $\Delta E$ as $T \to 0$. Thus written (18) is purely thermodynamic and is in principle due to Nernst. Thermodynamics can predict nothing concerning the values of the chemical constant $j$, but asserts only that there is one chemical constant for each gaseous molecular species, and that this same constant will occur in all chemical equilibria in which that particular species takes part. This is the reason for the name *chemical constant*. Statistical mechanics gives us the values of these constants.

All the formulae of this section, except those for monatomic molecules, involve the assumption that the rotational degrees of freedom are classical. We postpone to § 524 a discussion of how to amend them when this condition is not fulfilled.

**§ 511. Chemical constants of isotopic mixtures.** If we are interested in equilibria between isotopes, each isotope must be treated as a separate chemical species and there is no special difficulty. We have already in § 509 given an example of such a problem. More often we shall not be interested in the isotopic composition, and it will be more convenient to ignore the existence of isotopes. We shall now explain how this may be done.

Consider for example the parallel reactions

$$\mathrm{H}R+\mathrm{H}R \rightleftarrows \mathrm{H}_2 + R_2, \qquad (511,1)$$

$$\mathrm{D}R+\mathrm{D}R \rightleftarrows \mathrm{D}_2 + R_2, \qquad (511,2)$$

$$\mathrm{H}R+\mathrm{D}R \rightleftarrows \mathrm{HD} + R_2, \qquad (511,3)$$

where H, D denote the isotopes hydrogen, deuterium, while $R$ denotes a single atomic species such as $^{35}\mathrm{Cl}$. If we define the equilibrium constants of these reactions by

$$p_{\mathrm{H}_2} p_{R_2}/(p_{\mathrm{H}R})^2 = K_{\mathrm{HH}}, \qquad (511,4)$$

$$p_{\mathrm{D}_2} p_{R_2}/(p_{\mathrm{D}R})^2 = K_{\mathrm{DD}}, \qquad (511,5)$$

$$p_{\mathrm{HD}} p_{R_2}/p_{\mathrm{H}R} p_{\mathrm{D}R} = K_{\mathrm{HD}}, \qquad (511,6)$$

and express these equilibrium constants in terms of partition functions, we find that the symmetry numbers of $H_2$, $D_2$ and $R_2$ contribute factors 1/4, 1/4, 1/2, to $K_{\mathrm{HH}}$, $K_{\mathrm{DD}}$, $K_{\mathrm{HD}}$ respectively. Hence we have the approximations

$$K_{\mathrm{HH}} \simeq K_{\mathrm{DD}} \simeq \tfrac{1}{2} K_{\mathrm{HD}}, \qquad (511,7)$$

the inexactness of the equalities being due to differences of mass, moments of inertia, vibrational frequencies, and residual vibrational energies. If we do not wish to distinguish explicitly between the isotopes H, D, the effective equilibrium constant is defined by

$$K = (p_{\mathrm{H}_2}+p_{\mathrm{D}_2}+p_{\mathrm{HD}})\, p_{R_2}/(p_{\mathrm{H}R}+p_{\mathrm{D}R})^2. \qquad (511,8)$$

From (4–8) we deduce that

$$K \simeq K_{\mathrm{HH}} \simeq K_{\mathrm{DD}} \simeq \tfrac{1}{2} K_{\mathrm{HD}}, \qquad (511,9)$$

and so the effective chemical constant $j$ is approximately given by

$$j \simeq j_{\mathrm{HH}} \simeq j_{\mathrm{DD}} \simeq j_{\mathrm{HD}} - \log 2. \qquad (511,10)$$

We can write (10) alternatively in the form

$$j \simeq j_{\mathrm{HH}} \simeq j_{\mathrm{DD}} \simeq j'_{\mathrm{HD}}, \qquad (511,11)$$

where $j'_{\mathrm{HD}}$ is a fictitious chemical constant, obtained by applying to HD the formula for the chemical constant of a molecule with symmetry number 2.

To obtain a more accurate value of the effective chemical constant $j$ we take a weighted average of the true chemical constants $j_{\mathrm{HH}}$, $j_{\mathrm{DD}}$, and the fictitious chemical constant $j'_{\mathrm{HD}}$:

$$j = x_{\mathrm{H}_2} j_{\mathrm{H}_2} + x_{\mathrm{D}_2} j_{\mathrm{D}_2} + x_{\mathrm{HD}} j'_{\mathrm{HD}}, \qquad (511,12)$$

where $x_{H_2}$, $x_{D_2}$, $x_{HD}$ are the relative amounts of $H_2$, $D_2$, HD expressed as fractions of $H_2+D_2+HD$. As the values of $j_{H_2}, j_{D_2}, j_{HD}$ do not differ greatly from one another, we require only rough values of $x_{H_2}$, $x_{D_2}$, $x_{HD}$ in (12). But in § 509 we showed that

$$x_{H_2}x_{D_2}/x_{HD}^2 \simeq \tfrac{1}{4}. \qquad (511, 13)$$

If $1-\xi$ and $\xi$ are the fractional abundances of H and D atoms regardless of the state of combination, then (13) is equivalent to the relations

$$x_{H_2} : x_{HD} : x_{D_2} = (1-\xi)^2 : 2\xi(1-\xi) : \xi^2. \qquad (511, 14)$$

We may therefore write in place of (12)

$$j = (1-\xi)^2 j_{H_2} + 2\xi(1-\xi)\, j'_{HD} + \xi^2 j_{D_2}. \qquad (511, 15)$$

Thus in the formula for $j$ we must use an effective mass $m$ defined by

$$\log m = (1-\xi)^2 \log m_{H_2} + 2\xi(1-\xi) \log m_{HD} + \xi^2 \log m_{D_2}, \quad (511, 16)$$

and an effective moment of inertia $A$ defined by

$$\log A = (1-\xi)^2 \log A_{H_2} + 2\xi(1-\xi) \log A_{HD} + \xi^2 \log A_{D_2}. \quad (511, 17)$$

Exactly analogous considerations apply to other isotopic mixtures. We have therefore the simple rule, that, as long as we are not interested in the separation of isotopes, we may ignore their existence, except in so far as we use correctly averaged values for the properties of the isotopic mixture.

**§ 512. Equilibrium between a crystal and its vapour.** We turn now to the equilibrium between a crystal and its vapour. The thermodynamic condition for equilibrium is

$$\mu^G = \mu^K, \qquad (512, 1)$$

where the superscript $G$ refers to the gaseous phase, and the superscript $K$ to the crystal phase. If then we can by statistical methods evaluate $\mu^G$ and $\mu^K$, the equilibrium is statistically determined. We have already given formulae for $\mu^G$ and $\mu^K$, and the equilibrium is correctly given by using them. But we must not forget that these values were obtained from $F^G$ and $F^K$, which in turn were arbitrarily defined by (225, 4) and (408, 1) respectively. It is true that we proved that $F^G$, $F^K$ depend on $T$ and on $V$ in exactly the same way as the thermodynamic free energy, but their dependence on $N$ was there assigned quite arbitrarily. To complete the statistical argument we should determine *a priori* the statistical condition for equilibrium between crystal and vapour, and then show that this can be put into the form (1) with the values of $F^G$, $F^K$ and so of $\mu^G$, $\mu^K$ hitherto assumed. To this we now proceed.

We consider an assembly of total volume $V$ and total energy $E$ containing altogether $N$ molecules. We commence by considering an example of the

assembly, in which $n$ of the molecules are in the gas and $N-n$ are in the crystal. Let $f(z)$ be the partition function for gaseous molecules, and let $\kappa(z)$ be the partition function per molecule in the crystal as defined in § 408. Then by the usual method of counting complexions we find, to the accuracy with which classical statistics are applicable, that the total number of complexions for this example of the assembly is equal to the coefficient of $x^n z^E$ in

$$\{\kappa(z)\}^{N-n}\exp\{xf(z)\}, \tag{512, 2}$$

in which $\kappa(z)$ and $f(z)$ must refer to the same energy zero.

If we neglect compressibility, the volume $\mathsf{V}$ per molecule in the crystal has a definite value at each temperature. The volume of the vapour phase for the particular example of the assembly which we are considering will be $V-(N-n)\mathsf{V}$. We therefore know that $f(z)$ will contain $V-(N-n)\mathsf{V}$ as a factor, and will otherwise be independent of $V$, $N$ and $n$. We therefore define $\phi(z)$ by

$$f(z) = \phi(z)\{V-(N-n)\mathsf{V}\}, \tag{512, 3}$$

and $\phi(z)$ is then independent of $V$, $N$ and $n$. The total number of complexions for the example of the assembly being considered is then the coefficient of $x^n z^E$ in

$$\{\kappa(z)\}^{N-n}\exp\{x\phi(z)\,V-(N-n)\,x\phi(z)\,\mathsf{V}\}, \tag{512, 4}$$

or alternatively the coefficient of $x^N z^E$ in

$$\exp\{(N-n)\log[x\kappa(z)]+x\phi(z)\,V-(N-n)\,x\phi(z)\,\mathsf{V}\}. \tag{512, 5}$$

Finally, in an assembly in which evaporation and condensation are proceeding freely, all values of $n$ from 0 to $N$ are possible, and the total number of complexions for the assembly could be obtained by summation over all possible examples. This summation is, however, neither convenient nor necessary.

All average properties of the assembly would be known if we knew the average value of $n$. For it can be shown that this knowledge would completely fix the average volumes and energies of the gas and crystal separately. The average properties of each would then be determined according to the formulae of Chapters III and IV respectively. Thus the whole problem is reduced to determining the average value of $n$. In § 515 we shall briefly outline how this can be done. Anticipating this we shall here merely quote the result and examine its consequences.

It can be shown that the average value of $n$ is that value of $n$ which makes the expression (5) have a maximum, when $z$ is replaced by $\vartheta$ or $e^{-1/kT}$, and $x$ by the value of $\lambda$ in the gas corresponding to this value of $n$. It can also be shown that this value of $n$ is determined by the condition that the coefficient of $(N-n)$ in (5) should vanish, when $z$ is replaced by $\vartheta = e^{-1/kT}$, and $x$ by the

value of $\lambda$ in the gas. If we provisionally accept this, then the average state of the assembly is determined by the relation

$$\log\{\lambda^G \kappa(\vartheta)\} = \lambda^G \phi(\vartheta)\, V. \qquad (512, 6)$$

But from the definition (3) of $\phi(z)$ and from (225, 3)

$$\lambda^G \phi(\vartheta) = \bar{n}/V^G, \qquad (512, 7)$$

where $\bar{n}$ is the average number of molecules in the gas and $V^G$ is the average volume of the gas. Substituting (7) into (6) we obtain

$$\log \lambda^G = -\log \kappa + \frac{\bar{n}}{V^G} V. \qquad (512, 8)$$

Before interpreting this formula we shall derive an extended form of it.

**§ 513. Crystal and vapour in the presence of inert gases.** We consider an assembly consisting of a crystal composed of molecules $A$, and a gaseous phase containing molecules of $A$ and of an inert gas $B$, which has no interaction with the crystal other than exerting a pressure on it by molecular bombardment. Let the total number of $A$ molecules be $N$ and the number of $B$ molecules be $N'$. If the $B$ molecules have a partition function $f'(z)$, and we define $\phi'(z)$ by the relation

$$f'(z) = V^G \phi'(z), \qquad (513, 1)$$

then the number of complexions for the example of the assembly, when the number of molecules $A$ in the gas phase is $n$, is given by the coefficient of $x^N y^{N'} z^E$ in

$$\exp\{(N-n)\log[x\kappa(z)] + x\phi(z)\, V - (N-n)\, x\phi(z)\, V$$
$$+ y\phi'(z)\, V - (N-n)\, y\phi'(z)\, V\}. \qquad (513, 2)$$

This expression is the obvious extension of (512, 5). It is to be observed that the partition function $f'(z)$ depends on $n$ through the factor $V^G$, but $\phi'(z)$ is independent of $N$, $N'$, $n$. The average value of $n$ is again given by the condition that when we replace $z$ by $\vartheta = e^{-1/kT}$, $x$ by $\lambda_A$, and $y$ by $\lambda_B$, the coefficient of $(N-n)$ in (2) must vanish for the values of $\lambda_A$, $\lambda_B$ corresponding to the required average value of $n$. This condition is

$$\log\{\lambda_A \kappa(\vartheta)\} = \lambda_A \phi(\vartheta)\, V + \lambda_B \phi'(\vartheta)\, V. \qquad (513, 3)$$

Using the definitions of $\phi$ and $\phi'$ and (225, 3), this becomes

$$\log \lambda_A = -\log \kappa + \frac{\bar{n} + N}{V^G} V, \qquad (513, 4)$$

or using the equation of state of perfect gases

$$\log \lambda_A = -\log \kappa + PV/kT, \qquad (513, 5)$$

where $P$ is the total pressure of the gas.

**§ 514. Thermodynamic interpretation.** We have derived formula (513, 5) by purely statistical reasoning, and can now translate it into thermodynamic terms. It must be remembered that the value of $\lambda_A$ occurring in (513, 5) is the value of $\lambda_A$ for a gas having the composition of the actual vapour in equilibrium with the crystal. To emphasize this point we add the superscript $G$ to $\lambda_A$ and can now drop the subscript $A$. We thus rewrite (513, 5) as

$$\log \lambda^G = -\log \kappa + PV/kT. \tag{514, 1}$$

The right-hand side of (1) is determined entirely by the temperature of, and the total pressure on, the crystal. We may therefore regard (1) as the condition for equilibrium between crystal and vapour recalling the thermodynamic condition

$$\mu^G = \mu^K, \tag{514, 2}$$

since in (2) as in (1) the left-hand side is a function of the state of the gas, and the right-hand side a function of the state of the crystal. We can now go further and identify (1) with (2) if we define the partial potentials $\mu^G$, $\mu^K$ in terms of statistical quantities by the relations

$$\mu^G = kT \log \lambda^G, \tag{514, 3}$$

$$\mu^K = -kT \log \kappa + PV. \tag{514, 4}$$

But (3) and (4) are exactly the definitions which we have already used tentatively in Chapters III and IV. We have now completed the justification for these definitions, by showing that they enable us to arrive at the usual thermodynamic conditions of equilibrium (2) from purely statistical considerations.

For some purposes it is convenient to introduce a statistical quantity $\lambda^K$ for the crystal related to $\kappa$ by

$$\log \lambda^K = -\log \kappa + PV/kT. \tag{514, 5}$$

We then have in both the gas and the crystal the same relation between $\mu$ and $\lambda$,

$$\mu = kT \log \lambda, \tag{514, 6}$$

and the condition for equilibrium between vapour and crystal can be expressed in the form

$$\lambda^G = \lambda^K. \tag{514, 7}$$

We accordingly call $\lambda$ the absolute activity in either phase.

From (4) we derive for the contribution of each molecule to the free energy of the crystal

$$F = \mu - PV = -kT \log \kappa, \tag{514, 8}$$

in agreement with formula (408, 14). To complete the justification of this formula, introduced in Chapter I as a tentative assumption, we have had to consider variations in the number of molecules in the crystal. This could not conveniently be done at an earlier stage.

**§ 515. Mathematical derivation of the results of the preceding sections.** We start with a few words of further explanation of (512, 5) and (513, 2). According to the general principles of short cut methods for enumerating complexions laid down in Chapter I, in order to enumerate the complexions contributed by all examples of the assembly, in which there are just $N-n$ molecules in the crystal, it is sufficient to treat the crystal as one permanent system of $N-n$ molecules, and to exact the proper symmetry requirements for the remaining $n$ non-localized molecules in the vapour phase. With the notation of § 512 it is at once clear that the number of complexions is strictly the coefficient of $x^n z^E$ in

$$\{\kappa(z)\}^{N-n}\,\Pi_r\,(1 \pm xz^{\epsilon_r})^{\pm\varpi_r}. \tag{515, 1}$$

This number is also the coefficient of $x^N z^E$ in

$$\exp\{(N-n)\log[x\kappa(z)] + \Sigma_r\,\varpi_r \log(1 \pm xz^{\epsilon_r})^{\pm 1}\}. \tag{515, 2}$$

Now when the classical approximation to the statistics of the gas phase is sufficiently accurate, all the terms $\log(1 \pm xz^{\epsilon_r})^{\pm 1}$ reduce effectively to $xz^{\epsilon_r}$, and this reduction may be made from the start. We therefore find that the total number of complexions contributed by examples with $n$ molecules in the gas phase is the coefficient of $x^N z^E$ in

$$\exp\{(N-n)\log[x\kappa(z)] + xf(z)\},$$

that is in

$$\exp\{(N-n)\log[x\kappa(z)] + x\phi(z)\,V - (N-n)\,x\phi(z)\,v\}, \tag{515, 3}$$

where $f(z)$ is the gaseous partition function for each molecule when there are $n$ of them in the gas, so that $f(z) = \{V-(N-n)\,v\}\,\phi(z)$ as postulated in § 512. Exactly similar arguments establish (513, 2). It is assumed in this argument that $v$ is correctly known *a priori*.

If we denote this number of complexions by $C_n$ we have therefore, by using Cauchy's theorem twice,

$$C_n = \frac{1}{(2\pi i)^2}\iint \frac{dx\,dz}{x^{N+1}z^{E+1}} \exp\{(N-n)\log[x\kappa(z)] + x\phi(z)\,V - (N-n)\,x\phi(z)\,v\}. \tag{515, 4}$$

For the complete set of complexions $C$ we have

$$C = \Sigma_n\,C_n, \tag{515, 5}$$

and by the fundamental hypothesis of statistical mechanics

$$C\overline{n} = \Sigma_n\,nC_n. \tag{515, 6}$$

Now it can be proved* rigorously that a sufficiently accurate approximation for $\log C_n$ is obtained by replacing the integral (4) by the value at the col

* See *S.M.* § 5 41.

of the factor multiplying $dx\,dz/xz$ in the integrand. This approximation gives

$$\log C_n = (N-n)\log\{\lambda\kappa(\vartheta)\} + \lambda\phi(\vartheta)\{V-(N-n)\,v\} - N\log\lambda - E\log\vartheta, \tag{515, 7}$$

where $\vartheta$ and $\lambda$ are the unique roots of the pair of equations

$$\vartheta\frac{\partial\log C_n}{\partial\vartheta} = \lambda\{V-(N-n)\,v\}\,\vartheta\frac{\partial\phi(\vartheta)}{\partial\vartheta} + (N-n)\,\vartheta\frac{\partial\log\kappa(\vartheta)}{\partial\vartheta} - E = 0, \tag{515, 8}$$

$$\lambda\frac{\partial\log C_n}{\partial\lambda} = \lambda\{V-(N-n)\,v\}\,\phi(\vartheta) + (N-n) - N = 0. \tag{515, 9}$$

The parameters $\vartheta$ and $\lambda$ so determined are functions of $n$.

We now seek to evaluate $C$ and $C\bar{n}$ by searching for the maximum value of $\log C_n$ as given by equations (7), (8) and (9). It must occur where

$$d\log C_n/dn = 0,$$

that is where
$$\left[\frac{\partial}{\partial n} + \frac{\partial\vartheta}{\partial n}\frac{\partial}{\partial\vartheta} + \frac{\partial\lambda}{\partial n}\frac{\partial}{\partial\lambda}\right]\log C_n = 0. \tag{515, 10}$$

Owing to the subsidiary conditions (8) and (9) this reduces to

$$\left(\frac{\partial}{\partial n}\log C_n\right)_{\vartheta,\lambda} = 0, \tag{515, 11}$$

or
$$-\log\{\lambda\kappa(\vartheta)\} + \lambda v\phi(\vartheta) = 0. \tag{515, 12}$$

It can be shown that (12) determines a unique maximum among the terms of the series at $n = n^*$. On referring to equation (9) we see that it is also true that at this maximum

$$\lambda = n^*/\{V-(N-n^*)\,v\}\,\phi(\vartheta) = n^*/V^G\phi(\vartheta) = n^*/f^G(\vartheta), \tag{515, 13}$$

the superscript $G$ denoting, as usual, the value in the gaseous phase. From (13) we see that $\lambda$ in (12) has the value characteristic of the gas phase for the corresponding values $n^*$ of $n$ and $V^G$, provided that $\vartheta$ may be identified with $e^{-1/kT}$. This identification may be made at once, if we consider a more inclusive assembly which contains, besides the complex crystal-vapour system, an ordinary gas of molecules, or a set of oscillators constant in number, capable of exchanging energy with the crystal-vapour system, but composed of entirely distinct molecules. The equilibrium state of this assembly will be governed by a common value of the parameter $\vartheta$, and, in the part of the assembly distinct from the crystal-vapour system, we may suppose that the identification of $\vartheta$ and $e^{-1/kT}$ has already been made.

It can be proved further that $n = n^*$ corresponds to such a strong maximum among the terms of the series (5), that the terms in the immediate neighbourhood of this value make the dominant contribution to $C$. Similarly the terms in this neighbourhood in series (6), or any similar series with a

slowly varying extra factor such as $n$, make the dominant contribution. It follows at once that

$$\bar{n} = n^*, \tag{515, 14}$$

and further that any other average quantity, such as $\bar{E}^G$ or $\bar{E}^K$, has a value derived entirely from these terms, and therefore corresponds to the ordinary values obtained when $n$ is fixed at $\bar{n} = n^*$, as we have already assumed. The statistical proof of the results used in § 512 is thus completed, and those of § 513 may be established in exactly the same way.

**§ 516. Vapour pressure of a crystal.** We can now obtain an explicit formula for the vapour pressure of a crystal, by substituting into the thermodynamic equilibrium condition

$$\mu^G = \mu^K \tag{516, 1}$$

the values for $\mu^G$ and $\mu^K$ obtained by statistical mechanics.

For $\mu^G$ we have by (510, 9)

$$\mu^G/kT = \epsilon_0/kT + \log p - (C_p^0/k)\log T - \Sigma_v \log q_v(T) - j - \Sigma \log \rho, \tag{516, 2}$$

while for $\mu^K$ we have by (514, 4)

$$\mu^K/kT = -\log \kappa(T) + PV/kT. \tag{516, 3}$$

We must now consider more carefully the form of $\kappa(T)$. In all formulae where evaporation and condensation are permitted it is of course essential that the gaseous and crystal partition functions should be referred to the same energy zero. We therefore have for the crystal, using the notation of § 415,

$$\kappa(T) = e^{-(\epsilon_0 - \chi)/kT}\,\alpha(T)\,j(T), \tag{516, 4}$$

where $\epsilon_0$ denotes the energy of the lowest quantum state of a gaseous molecule, and $\chi$ denotes the excess of this energy over that of a molecule in the crystal in its lowest quantum state; $\alpha(T)$ is the partition function per molecule for the acoustical modes; $j(T)$ is the partition function for the internal degrees of freedom of the molecule in the crystal.† We can further usually assume that, in the accessible temperature range, the only factors of $j(T)$ which are temperature dependent are those from the internal vibrational modes. We may then write

$$j(T) = Q(T)\,o\,\varpi_0^K\,\Pi\rho, \tag{516, 5}$$

where $Q(T)$ is the partition function for all the internal vibrations, $\varpi_0^K$ is the weight of the lowest electronic state, and $\Pi\rho$ is the product of the nuclear weights. Finally $o$ is an orientational factor, usually unity; it can, however, differ from unity if there are several distinguishable orientations of the molecule in the crystal with effectively equal energies. We shall have much

† There should be no confusion between $j(T)$ in formulae (4) and (5) and the symbol $j$ for the chemical constant.

to say about $o$, but at this stage all we need emphasize is that $o$, like $v_0^K$ and the $\rho$'s, is temperature independent.

If we now substitute (5) into (4), and then (4) into (3), we obtain

$$\frac{\mu^K}{kT} = \frac{\epsilon_0 - \chi}{kT} + \frac{PV}{kT} + \log\{\alpha(T)\,Q(T)\} + \log\{ov_0^K\,\Pi\rho\}. \qquad (516, 6)$$

If we now substitute (2) and (6) into (1), we obtain for the vapour pressure over the crystal

$$\log p = -\chi/kT + PV/kT + \{(C_P^0/k)\log T + \Sigma_v \log q_v(T)\}^G$$
$$- \{\log \alpha(T) + \log Q(T)\}^K + j^G - \log\{ov_0^K\}, \qquad (516, 7)$$

the nuclear weights again cancelling. This result is, as it must be, independent of the common energy zero used for the energy states in the crystal and in the gas. Superscripts $G$ and $K$ have been inserted to distinguish functions referring to the gas and the crystal respectively, but they will in future be dropped whenever there is no danger of confusion.

**§ 517. Vapour pressure constants.** We can translate (516, 7) into thermodynamic form as follows. We pointed out in § 510 that

$$\Sigma_v \log q_v^G(T) = \int_0^T \frac{dT_1}{T_1^2} \int_0^{T_1} \frac{C'(T_2)}{k}\, dT_2, \qquad (517, 1)$$

where $C'$ is defined by (510, 13). In an exactly similar way it can be shown that

$$\log\{\alpha(T)\,Q(T)\}^K = \int_0^T \frac{dT_1}{T_1^2} \int_0^{T_1} \frac{C^K(T_2)}{k}\, dT_2. \qquad (517, 2)$$

where $C^K$ is the molecular heat capacity of the crystal,* provided that the integral converges, and no degrees of freedom other than the acoustical and the internal vibrations contribute to $C^K$. We shall consider these restrictions later. Substituting (1) and (2) into (516, 7) we obtain

$$\log p = -\chi/kT + PV/kT + \frac{C_P^0}{k}\log T + \int_0^T \frac{dT_1}{T_1^2} \int_0^{T_1} \frac{C' - C^K}{k}\, dT_2 + i, \quad (517, 3)$$

where

$$i = j - \log ov_0^K. \qquad (517, 4)$$

$i$ is called the *vapour pressure constant.*

**§ 518. Relation between vapour pressure constants and chemical constants.** Formula (517, 3) for the vapour pressure of a crystal and formula (510, 18) for the equilibrium constant of a gaseous equilibrium are both obtainable by pure thermodynamics, and were effectively first so obtained by Nernst. But classical thermodynamics can predict nothing

* Our choice of energy zero and weight factors is such that $\alpha(0) = Q(0) = 1$.

about the values of the two integration constants, namely the vapour pressure constant $i$ in the former case, and the chemical constant $j$ in the latter. Statistical mechanics, however, predicts the values of both, and in particular the relation between them,

$$i = j - \log o v_0^K. \tag{518, 1}$$

For the majority of crystals $o$ and $v_0^K$ are both unity, in which case $i$ and $j$ are identical. The two constants are, however, in principle different* and must not be confused.

We shall see that one version of Nernst's heat theorem is equivalent to the assertion that

$$o v_0^K = 1, \tag{518, 2}$$

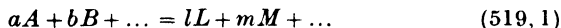
which leads to

$$i = j. \tag{518, 3}$$

If this were valid for all crystals, there would be no necessity to continue to distinguish between the vapour pressure constants $i$ and the chemical constants $j$ as they would be equal. We shall discuss the conditions for the validity of (2) in great detail in §§ 536–539. Meanwhile we shall continue to distinguish between $i$ and $j$.

**§ 519. Heterogeneous reactions.** We have so far considered homogeneous gaseous equilibria and equilibria between a single crystal and a vapour phase. Any heterogeneous equilibrium between several pure crystal phases and a vapour phase can be regarded as a superposition of the two types of equilibrium already discussed. There is therefore no need to discuss the more general type of heterogeneous equilibrium in detail. We shall refer only to one type of special interest, namely an equilibrium between pure crystals only, the vapour phase not occurring in the equilibrium equation being discussed. This does not mean that the presence of a vapour phase is excluded, but merely that every species taking part in the chemical process being discussed is present in a pure crystalline phase as well as in the vapour.

Let us consider the process

$$aA + bB + \ldots = lL + mM + \ldots \tag{519, 1}$$

occurring between crystalline phases, and let us use the operator $\Delta$ to denote the increase in the value of some function for the whole assembly when $a$ molecules $A$, $b$ molecules $B$, ... are isothermally and at constant pressure replaced by or changed into $l$ molecules $L$, $m$ molecules $M$, .... We have then

$$\Delta \Sigma \mu = \Delta \Sigma (\epsilon^0 - \chi) + P \Delta \Sigma V - kT \Delta \Sigma \log\{\alpha(T)\, Q(T)\} - kT \Delta \Sigma \log o v_0^K. \tag{519, 2}$$

* Cf. Eucken and Fried, *Zeit. Phys.* **29**, 36 (1924).

In thermodynamic notation this becomes

$$\Delta \Sigma \mu = \Delta E^0 + P\Delta \Sigma V - T\int_0^T \frac{dT_1}{T_1^2}\int_0^{T_1} \Delta \Sigma C dT_2 - kT\Delta \Sigma \log ov_0^K, \quad (519,3)$$

where $\Delta E^0$ is the limiting value as $T \to 0$ of $\Delta E$ for the reaction between the crystals. Formulae (3) is derivable from pure thermodynamics* except for the definite value,

$$\Delta \Sigma \log ov_0^K = \Delta \Sigma (j - i), \quad (519,4)$$

of the coefficient of $-kT$ in the last term.

The value of $\Delta \Sigma \mu$ can be determined experimentally at a given temperature $T$ by electromotive force measurements, provided the process can be made to take place reversibly in such a manner as to give an electric cell. Alternatively one can measure the transition temperature, that is the temperature at which the direction of the naturally occurring process becomes reversed. At this temperature $\Delta \Sigma \mu$ is zero. All the terms on the right of (3) except the last can be determined by calorimetric and density measurements. Consequently, when these data have been obtained, a determination of the transition point, or a measurement of electromotive force, fixes the experimental value of the integration constant (4).

As already mentioned, for the majority of crystals $ov_0^K$ is certainly unity, and the integration constant (4) is then zero. The vanishing of (4) is the statistical equivalent of Nernst's heat theorem.

§ 520. **Perfect mixed crystals.** We have hitherto in this chapter considered only simple crystals composed of one type of molecule. The formulae are easily extended to mixed crystals in the special case that the different molecules forming the mixed crystal are very similar. This case has been discussed in § 415, where we found that the partition function $K(T)$ for a crystal containing $N_A$ molecules $A$ and $N_B$ molecules $B$ has the form

$$K(T) = \frac{(N_A + N_B)!}{N_A!\,N_B!}\{\alpha(T)\}^{N_A+N_B}\{e^{\chi_A/kT} j_A(T)\}^{N_A}\{e^{\chi_B/kT} j_B(T)\}^{N_B}. \quad (520,1)$$

The essential approximation is that the acoustical partition function $\alpha(T)$, the internal partition functions $j_A(T)$, $j_B(T)$ and the energies $\chi_A$, $\chi_B$ should all be independent of the ratio $N_A : N_B$, and of the different configurations of the molecules in the lattice. It may safely be assumed to be accurate for a mixture of isotopes, which is the case to which we want to apply (1).

The free energy of the whole ideal mixed crystal is given by

$$\begin{aligned} F &= -kT\log K(T) \\ &= -N_A kT \log\{e^{\chi_A/kT}\alpha(T)\, j_A(T)\,(N_A+N_B)/N_A\} \\ &\qquad - N_B kT\log\{e^{\chi_B/kT}\alpha(T)\, j_B(T)\,(N_A+N_B)/N_B\}, \quad (520,2) \end{aligned}$$

* See *M.T.* Chapter XIV.

using Stirling's approximation for $\log(N_A+N_B)!$, $\log N_A!$ and $\log N_B!$. For the Gibbs function $G$ we have

$$G = -N_A kT\{\log e^{\chi_A/kT}\alpha(T)\,j_A(T)\,(N_A+N_B)/N_A\}$$
$$-N_B kT\{\log e^{\chi_B/kT}\alpha(T)\,j_B(T)\,(N_A+N_B)/N_B\}+PV, \quad (520,3)$$

and so for the partial potentials

$$\mu_A = PV_A-\chi_A-kT\log\{\alpha(T)\,j_A(T)\,(N_A+N_B)/N_A\}, \quad (520,4)$$

$$\mu_B = PV_B-\chi_B-kT\log\{\alpha(T)\,j_B(T)\,(N_A+N_B)/N_B\}. \quad (520,5)$$

If we compare (4) with the partial potential of $A$ in the pure crystal we obtain

$$\mu_A(T,P) = \mu_A^0(T,P)+kT\log\frac{N_A}{N_A+N_B}, \quad (520,6)$$

where $\mu_A(T,P)$ denotes the partial potential in the perfect mixed crystal, and $\mu_A^0(T,P)$ the partial potential in the pure crystal at the same temperature and pressure.

The extension to ideal mixed crystals of more than two molecular species is obviously

$$\mu_A(T,P) = \mu_A^0(T,P)+kT\log x_A, \quad (520,7)$$

where $x_A$ denotes the molecular fraction of $A$ in the crystal defined by

$$x_A = N_A/(N_A+N_B+\ldots). \quad (520,8)$$

The partial vapour pressure of $A$ over the ideal mixed crystal is obtained by equating the partial potentials of $A$ in the crystal and in the vapour. The result obtained is

$$p_A(T,P) = p_A^0(T,P)\,x_A, \quad (520,9)$$

where $p_A(T,P)$ is the partial pressure of $A$ over the ideal mixed crystal and $p_A^0(T,P)$ is the partial pressure of $A$ over the pure crystal at the same temperature and total pressure.

By comparing the value given by (2) for the free energy of the perfect mixed crystal with the values for the crystals of the single component substances, we find for the free energy decrease $-\Delta F$ on mixing

$$-\Delta F = kT\left\{N_A\log\frac{N_A+N_B}{N_A}+N_B\log\frac{N_A+N_B}{N_B}\right\}>0. \quad (520,10)$$

The corresponding entropy increase $\Delta S$, usually called the entropy of mixing, is

$$\Delta S = -\frac{\partial\Delta F}{\partial T} = k\left\{N_A\log\frac{N_A+N_B}{N_A}+N_B\log\frac{N_A+N_B}{N_B}\right\}>0. \quad (520,11)$$

We notice that the entropy of mixing of a perfect mixed crystal is given by the same formula as (505, 12) for the entropy of mixing of two perfect gases at constant total pressure.

**§ 521. Vapour pressure of a crystal composed of isotopes.** For a crystal composed of isotopes we see by using (520, 9) that the partial pressure $p_i$ of the isotope $i$ is given by

$$p_i = x_i p_i^0, \qquad (521, 1)$$

where $p_i^0$ is the partial pressure of the isotope $i$ over its pure crystalline phase at the same temperature and total external pressure. The total vapour pressure $p$ of the crystal is given by

$$p = \Sigma_i p_i = \Sigma_i x_i p_i^0. \qquad (521, 2)$$

This formula is exact for ideal mixed crytals, and so practically exact for isotopes. It is, however, inconvenient to use, and since the differences between $p_i$ for various isotopes are in the most unfavourable case of $H_2$ and $D_2$ only one part in seven, we may replace (2) by the approximation

$$\log p = \Sigma_i x_i \log p_i, \qquad (521, 3)$$

with an error less than 1 % in this most unfavourable case. We then obtain for the vapour pressure of the crystal

$$\log p = -\frac{\chi}{kT} + \frac{PV}{kT} + \frac{C_P^0}{k}\log T + \int_0^T \frac{dT_1}{T_1^2}\int_0^{T_1} \frac{C' - C^K}{k}\, dT_2 + i, \qquad (521, 4)$$

where $C_P^0$, $V$ have the same values for all the isotopes, while $\chi$, $C'$, $C^K$, $i$ are taken as weighted averages of the values $\chi_i$, $C_i'$, $C_i^K$, $i_i$ for the several isotopes according to the rules

$$\chi = \Sigma_i x_i \chi_i, \qquad (521, 5)$$

$$C' = \Sigma_i x_i C_i', \qquad (521, 6)$$

$$C^K = \Sigma_i x_i C_i^K, \qquad (521, 7)$$

$$i = \Sigma_i x_i i_i. \qquad (521, 8)$$

Since the values of $\chi$, $C'$, $C^K$ are determined directly by calorimetric measurements, it is the formula for $i$ that has particular interest.

We see that formula (8) relates the vapour pressure constant of the isotopic mixture to those of the pure single isotopes. Now the vapour pressure constants $i_i$ of the isotopic molecules may differ from one another owing to differences of mass $m_i$, differences of moments of inertia $A_i$, $B_i$, $C_i$, differences of the symmetry number $\sigma_i$ and differences of the weight $o_i v_{0,i}^K$ for the molecule in the crystal in its lowest energy state. The effect of differences in mass and moments of inertia is taken account of by using average values as already described in § 511 for the analogous chemical constants $j$. There is no reason to expect the electronic weight in the crystal to be different for different isotopes. There remain the symmetry number $\sigma_i$ of the gaseous molecule and the orientational weight $o_i$ in the crystal to be considered. These occur in the vapour pressure constant $i_i$, as the combination

$$-\log \sigma_i o_i. \qquad (521, 9)$$

Now it can be shown that as $\sigma_i$ changes from one isotope to another, $o_i$ varies in the inverse ratio to $\sigma_i$ and consequently (2) has the same value for all isotopes. Instead of giving a general proof of this we shall verify it for a simple example.

Let us compare the molecules $^{35}Cl\,^{35}Cl$, $^{37}Cl\,^{37}Cl$, $^{35}Cl\,^{37}Cl$. For the molecules $^{35}Cl\,^{35}Cl$, $^{37}Cl\,^{37}Cl$ the symmetry number $\sigma$ is 2, while for the molecule $^{35}Cl\,^{37}Cl$ it is 1. In the crystal on the other hand $o$ for $^{35}Cl\,^{37}Cl$ will have double the value for $^{35}Cl\,^{35}Cl$ or $^{37}Cl\,^{37}Cl$, because each molecule $^{35}Cl\,^{37}Cl$ can be reversed to give a physically distinct state of the crystal of effectively equal energy. Thus the product $\sigma o$ has the same value for the three types of molecules. It is easy to verify this in all more complicated cases.

We have then the simple rule for calculating the vapour pressure constant for a mixture of isotopes regarded as a simple substance. The molecular mass and moments of inertia are assigned values averaged according to the proportions of the several isotopes. Apart from this all the isotopes are treated as identical, and the isotopic nature of the mixture ignored.

**§ 522. Effects of ortho-para separations.** As we have already seen, molecular hydrogen (and deuterium) must frequently be treated as mixtures of two separate substances, para-hydrogen and ortho-hydrogen, owing to the slow rate of interchange between the para and the ortho states in the molecular form. There are special reasons why this division becomes prominent and important for hydrogen; the first is that its rotational degrees of freedom in the gas become non-classical at easily accessible temperatures; the second we shall examine in detail in § 531. The division, however, must undoubtedly occur for all other molecules of type $X_2$, and similar more complicated divisions will occur for polyatomic molecules of this or higher symmetry. In calculating chemical constants and vapour pressure constants for such substances we commonly entirely ignore these divisions, just as we ignore the separation of an element into isotopes. It is important to see why this neglect is in general justified. We shall be content to examine only the simplest case of a molecule $X_2$, in which the spin weight of each atomic nucleus is $\rho$.

(1) *The symmetrical molecule $X_2$ with equilibrium maintained between the para and ortho states.* We have already seen in § 508 that the nuclear symmetry requirements in the eigen functions can be completely taken care of in the gas phase by introducing the symmetry factor $1/\sigma = \frac{1}{2}$, and setting

$$r_n(T) = r(T)\,\tfrac{1}{2}\rho^2, \qquad (522,1)$$

provided the rotational degrees of freedom are classical or nearly classical.*

* This approximation is far more accurate than the classical approximation for $r(T)$ itself.

We shall now show that there is a similar simplification in the solid phase. In general, and certainly for all molecules $X_2$ no longer rotating in the crystal, each molecule $X_2$ will have, apart from nuclear spins, one para and one ortho state of least energy, these energies being effectively equal. These two states are the correct stationary states, which correspond to the two classical states provided by a single natural direction of equilibrium, and the possibility of turning the molecule end for end. The complete lowest energy terms in the partition function for the vibrations and nuclear orientations of each molecule in the crystal are therefore

$$\tfrac{1}{2}\rho(\rho-1)+\tfrac{1}{2}\rho(\rho+1)\,e^{\delta/kT}, \tag{522, 2}$$

where $\delta$ is the (negligible) energy difference between the para and ortho vibrational states. These two terms therefore reduce to the factor $\rho^2$, and the same factor occurs in all the higher vibrational states when these need to be retained. Thus the nuclear spins in the crystal still make the standard contribution to $\Pi\rho$, which could with equal propriety be regarded as the simple factor $\rho$ per atom in the crystal.

(2) *The symmetrical molecule $X_2$ when the para and ortho states must be regarded as effectively non-combining.* The above arguments apply only when there is full equilibrium between the para and ortho states of molecules of each type. This equilibrium in general is not preserved, and the gas and the crystal must each be treated as a perfect mixture of distinct sets of para and ortho molecules, exactly equivalent to an isotopic mixture. The rotational partition functions $r_p(T)$ and $r_o(T)$ for the two types of gaseous molecules consist one of the even and the other of the odd terms of $r(T)$, but provided the rotational degrees of freedom are classical or approximately classical we can assume that with a very high degree of accuracy*

$$r_p(T) = r_o(T) = \tfrac{1}{2}r(T). \tag{522, 3}$$

The two forms have therefore the same rotational partition function.

In the crystal phase the two forms, if librating, have sets of states which differ insignificantly in energy and lead therefore to equal partition functions. If effectively rotating, the same arguments apply as in the gas phase, so that in all cases and in both phases the rotational and vibrational partition functions of para and ortho molecules may be taken to be equal.

It follows from this equality, by reasoning exactly parallel to that of our discussion of isotopes in § 521, that the para and ortho forms occur in effectively the same proportions in the crystal and the gas. The para and ortho forms have nuclear spin weights $\tfrac{1}{2}\rho(\rho-1)$ and $\tfrac{1}{2}\rho(\rho+1)$ respectively, but these make equal contributions to the partition functions of each type

* These approximations are far more accurate than the classical formula for $r(T)$ itself.

in each phase and therefore also for the mixture. The entropy of mixing terms are also equal in both phases. We thus find again that the existence of para and ortho forms may be ignored.

This reasoning does not apply to $H_2$ and $D_2$, because their rotational degrees of freedom are far from classical. These molecules are also exceptional in another respect, and they are discussed separately in § 531.

This general absence of effect of ortho-para separations on phase equilibria, because taking account of them makes changes in the partition function equal in all phases, is even more complete than the general arguments above have indicated, and this complete absence of effect is worth recording in passing. Suppose we have a crystal of molecules $X_2$ composed of atoms of nuclear spin weight $\rho$. If we ignore entirely ortho-para separations and the association of atoms in pairs to form molecules, we should conclude that the partition function for the crystal of $2N$ atoms was of the form $\rho^{2N}K(T)$, where $K(T)$ takes account of all the normal modes of the solid. If we take account of ortho-para separations and all possible arrangements of the para and ortho molecules, we must regard the crystal as built up of a mixture of

$$N\tfrac{1}{2}\rho(\rho-1)/\rho^2 = N(\rho-1)/2\rho$$

para, and

$$N\tfrac{1}{2}\rho(\rho+1)/\rho^2 = N(\rho+1)/2\rho$$

ortho molecules. The partition function for the mixed crystal is then

$$\frac{N!}{\left[\dfrac{N(\rho-1)}{2\rho}\right]!\left[\dfrac{N(\rho+1)}{2\rho}\right]!}\left[\tfrac{1}{2}\rho(\rho-1)\right]^{\frac{N(\rho-1)}{2\rho}}\left[\tfrac{1}{2}\rho(\rho+1)\right]^{\frac{N(\rho+1)}{2\rho}}K(T). \quad (522, 4)$$

This differs from the earlier expression by the extra factor

$$\frac{N!\left[\dfrac{\rho-1}{2\rho}\right]^{\frac{N(\rho-1)}{2\rho}}\left[\dfrac{\rho+1}{2\rho}\right]^{\frac{N(\rho+1)}{2\rho}}}{\left[\dfrac{N(\rho-1)}{2\rho}\right]!\left[\dfrac{N(\rho+1)}{2\rho}\right]!}, \quad (522, 5)$$

which becomes unity for large $N$.

**§ 523. Molecular entropies of gas and crystal.** Many authors prefer to express their thermodynamic results in terms of entropy. We shall therefore derive the relevant formulae. For the partial potential of any single gas, if we do not assume the rotational and vibrational motions to be necessarily independent, we can write instead of (510, 9), (510, 10)

$$\mu^G(T, P) = \epsilon_0 + kT\log P - \tfrac{5}{2}kT\log T - kT\log rv(T)$$
$$- kT\log\left\{\frac{(2\pi m)^{\frac{3}{2}}k^{\frac{3}{2}}}{h^3}\frac{v_0\,\Pi\,\rho}{\sigma}\right\}, \quad (523, 1)$$

where $rv(T)$ denotes the rotational-vibrational partition function, including all terms regardless of their symmetry characters; these are taken care of by the symmetry number $\sigma$. The corresponding formula for the molecular entropy is

$$S^G(T,P) = -(\partial\mu^G/\partial T)_P$$
$$= -k\log P + \tfrac{5}{2}k\log T + k\log rv(T) + kT\frac{\partial \log rv(T)}{\partial T}$$
$$+ k\left[\log\left\{\frac{(2\pi m)^{\frac{3}{2}}k^{\frac{5}{2}}}{h^3}\frac{v_0\,\Pi\rho}{\sigma}\right\} + \frac{5}{2}\right]. \quad (523, 2)$$

For the crystal we have by (516, 3) and (516, 4)

$$\mu^K(T,P) = \epsilon_0 - \chi + PV - kT\log\{\alpha(T)\,j(T)\}, \quad (523, 3)$$

and for ordinary pressures ($PV \ll kT$)

$$\mu^K(T,0) = \epsilon_0 - \chi - kT\log\{\alpha(T)\,j(T)\}. \quad (523, 4)$$

Hence for the molecular entropy at ordinary pressure

$$S^K(T,0) = -(\partial\mu^K/\partial T)_{P\simeq 0} = k\log\{\alpha(T)\,j(T)\} + kT\frac{\partial\log\{\alpha(T)\,j(T)\}}{\partial T}. \quad (523, 5)$$

If we now make $T \to 0$ we have

$$\alpha(T) \to 1, \quad j(T) \to o v_0^K \Pi\rho, \quad (523, 6)$$

the last equation being in effect the definition of the orientational weight $o$. We thus obtain

$$S^K(0,0) = k\log\{o v_0^K \Pi\rho\}. \quad (523, 7)$$

If we now subtract (7) from (2) we obtain

$$S^G(T,P) - S^K(0,0) = -k\log P + \tfrac{5}{2}k\log T + k\log rv(T)$$
$$+ kT\frac{\partial\log rv(T)}{\partial T} + k\left[\log\left\{\frac{(2\pi m)^{\frac{3}{2}}k^{\frac{5}{2}}}{h^3}\frac{v_0^G}{\sigma o v_0^K}\right\} + \frac{5}{2}\right], \quad (523, 8)$$

the nuclear weights cancelling as usual.

Now the left side of (8) is directly determinable by calorimetric measurements apart from an inevitable extrapolation to zero temperature, about which we shall have more to say. For we have

$$S^G(T,P) - S^K(0,0) = \operatorname*{Lt}_{T^0\to 0}\int_{T^0}^{T}\frac{dq}{T}, \quad (523, 9)$$

where $dq$ is the element of heat absorbed, and the path of integration is any reversible one leading from the crystal at temperature $T^0$ and negligible pressure to the gas at temperature $T$ and pressure $P$. This path may, and usually will, pass through the liquid state. There may be two or more phase transitions on the way, and each will make its contribution to the integral. If now the energies of the molecule have been determined spectroscopically,

then $rv(T)$ and its temperature coefficient can be computed for each $T$, while $v_0^G$ and $\sigma$ are also determinable spectroscopically or otherwise. Thus everything on the right of (8) is known except $ov_0^K$. By comparison of the calorimetric and spectroscopic data one can determine the value of $ov_0^K$. If Nernst's heat theorem is obeyed, the value unity should be found.

§ 524. **Absolute entropy.** This is perhaps a suitable place to remind the reader that there is no physical significance in an absolute value of an entropy. It is only entropy differences between interconvertible states of an assembly that are physically significant. We have throughout used a convention such that, when every system is in its lowest quantum state, the contribution of each system to the entropy is

$$k \log \varpi_0, \tag{524, 1}$$

where $\varpi_0$ is the product of the weight of the lowest translational-rotational-vibrational-electronic state and the nuclear spin weight $\Pi\rho$. But, if we cared to do so, we might replace (1) by

$$k \log \varpi_0 + k \log \Pi a, \tag{524, 2}$$

where $a$ is an arbitrary constant characteristic of each atomic species, and the product is taken over all atoms in the system. So long as nuclear transformations are excluded, as they are excluded in all ordinary applications of thermodynamics, the new terms will cancel in all physically significant formulae, and no physical result will be affected. If we wished to include formulae valid for nuclear transformations, the degree of arbitrariness in the $a$'s would be greatly reduced. If all possible nuclear transformations were under consideration, one may presume that the arbitrariness would be reduced to three arbitrary factors $a_e$ for the electron, $a_p$ for the proton and $a_n$ for the neutron. Such considerations do not, however, normally interest us in terrestrial thermodynamics, and we are still too ignorant of the details of nuclear structure to be able to specify what the correct values of the $a$'s would be. There is, however, no reason to expect that the same value of $a$, namely unity, would be the correct value to assign to every type of nucleus. We thus see that there is nothing absolute about (1). Putting $a = 1$ for all nuclei is merely the simplest and most convenient convention allowable in the absence of nuclear transformations.

Returning to practical thermodynamics we may of course assign, if we please, the value zero to the entropy of all perfect crystals of a single pure isotope of a single element in its idealized state at the absolute zero of temperature, but even this has no theoretical significance on account of nuclear spin weights. For the purpose of calculating experimental results some conventional zero must be chosen, and the above choice or a similar

one is thus often convenient. But its conventional character will no longer be so likely to be overlooked that any importance will in future be attached to *absolute entropy*, an idea which has caused much confusion and been of very little assistance in the development of the subject.*

**§ 525. Extrapolation to absolute zero.** In deriving all our formulae we have assumed that we could select a temperature $T^0$ at which in the gas the vibrational degrees of freedom are unexcited, and the rotational degrees of freedom, except for monatomic molecules, are effectively classical. The formulae so obtained are then valid for all temperatures greater than $T^0$. At temperatures where the rotational degrees of freedom are nearly, but not entirely, classical, we can correct any formula by using a more accurate value for $r(T)$ than the classical value. For diatomic molecules we should according to (313, 4) use the approximation

$$\log r(T) = \log\frac{T}{\Theta_r} + \frac{1}{3}\frac{\Theta_r}{T} = \log\frac{8\pi^2 AkT}{h^2} + \frac{1}{3}\frac{h^2}{8\pi^2 AkT}, \quad (525, 1)$$

instead of the classical value given by the first term. Use of this more accurate form for $r(T)$ will introduce an extra term $-\frac{1}{3}\Theta_r/T$ into $\mu/kT$. If then we continue to use formula (510, 9), the effective chemical constant $j$ and the effective vapour pressure constant $i$ will not be true constants, but will each contain an extra term $\frac{1}{3}\Theta_r/T$. The magnitude of this correction will be discussed in §530. It is unimportant at ordinary temperatures for HCl, and is negligible for any molecule with a large moment of inertia.

With $H_2$, $D_2$, HD, owing to their small moments of inertia, one can perform experiments at temperatures at which the rotational degrees of freedom are far from classical and can even be unexcited. The formulae which we have given for diatomic molecules are not applicable at such temperatures, and we have to adopt a different procedure. At these temperatures the vibrational degree of freedom is unexcited and may be ignored. The procedure then adopted is to choose for $C_P^0$ the value given by

$$C_P^0/k = \tfrac{5}{2}, \quad (525, 2)$$

* To prevent all possibility of misunderstanding, we should perhaps mention that in deciding to call the $\lambda$'s "absolute activities" we are using the epithet "absolute" in an entirely different sense from that under discussion, the purpose being to contrast the $\lambda$'s with the relative activities $a$ used by the school of G. N. Lewis. If we compare two thermodynamic states denoted by single and double primes respectively, then

$$\mu' - \mu'' = kT \log \lambda'/\lambda''$$

is identically true, whereas the analogous

$$\mu' - \mu'' = kT \log a'/a''$$

is valid only if the two thermodynamic states have the same temperature.

and to define $C'(T)$ by

$$C'(T) = C_P(T) - \tfrac{5}{2}k \quad (T > T^0),$$
$$C'(T) = 0 \qquad (T < T^0), \tag{525, 3}$$

exactly as for a monatomic molecule, except that the temperature $T^0$ is now chosen in the range where the rotational degrees of freedom are unexcited. The value that has to be used for the vapour pressure constant $i$ in combination with this value of $C_P^0$ will be discussed in § 531.

Thus whether we define $C_P^0$ in the usual way, or in the exceptional way just described for $H_2$, HD and $D_2$, provided we choose an appropriate $T^0$ and define $C'(T)$ by

$$C'(T) = C_P - C_P^0 \quad (T > T^0),$$
$$C'(T) = 0 \qquad (T < T^0), \tag{525, 4}$$

the integral containing $C'(T)$ is

$$\int_0^T \frac{dT_1}{T_1^2} \int_0^{T_1} \frac{C'(T_2)}{k}\, dT_2 = \int_{T^0}^T \frac{dT_1}{T_1^2} \int_{T^0}^{T_1} \frac{C'(T_2)}{k}\, dT_2, \tag{525, 5}$$

and by the definition of $C'(T)$ there can be no question of the integral not converging.

We must now consider the convergence of the integral

$$\int_0^T \frac{dT_1}{T_1^2} \int_0^{T_1} \frac{C^K}{k}\, dT_2. \tag{525, 6}$$

Since one cannot perform experiments at the absolute zero, this integral must be regarded as an abbreviated notation for

$$\mathop{\mathrm{Lt}}_{T^0 \to 0} \int_{T^0}^T \frac{dT_1}{T_1^2} \int_{T^0}^{T_1} \frac{C^K}{k}\, dT_2, \tag{525, 7}$$

and in proceeding to the limit we are compelled to make an assumption or use a convention with regard to the behaviour of $C^K$ in the range 0 to $T^0$. We therefore proceed as follows. We choose for $T^0$ a temperature, in a range where $C^K$ is tending rapidly to zero according to some simple theoretical or semi-theoretical formula, such as that due to Debye described in Chapter IV. We then extrapolate to $T = 0$, using the convention that $C^K$ continues to obey this law. In other words $C^K$ is defined as follows:

For $T > T^0$: $C^K$ is the observed molecular heat capacity of the crystal.

For $T < T^0$: $C^K$ is defined by extrapolation according to the simplest formula with a theoretical basis that is verified to hold for $C^K$ when $T \simeq T^0$.

In the lower ranges of temperature there is no experimental value for the heat capacity, and we can only speculate as to what its value would be if the range became experimentally accessible. We shall postpone such speculation to a later stage. In anticipation we may mention here the conclusions we shall reach for substances, for which at present $\sigma v_0^K > 1$. When temperatures

much lower than $T^0$ become experimentally accessible, we may expect to find two alternative kinds of behaviour. (i) In some cases we shall find striking abnormalities in $C^K$ and, with a new much lower $T^0$, the new value of $ov_0^K$ will become unity. The important case of $H_2$ comes into this class. (ii) In other cases we shall find that the actual value of $C^K$ agrees closely with the extrapolated value here defined, and $ov_0^K$ is unaffected, remaining greater than unity. The measurements then in fact refer to a state of the solid which is strictly only metastable. There is then always a possibility that by performing the experiments extremely slowly the true equilibrium state may be attained. Different values of $C^K$ and $ov_0^K$ will then be found. But there are many cases in which the time required to reach true equilibrium is impossibly long at these low temperatures.

With the above definition of $C^K$, the integral (2), written as (1) for brevity, is completely defined and always convergent, because $C^K \to 0$ fairly rapidly when $T \to 0$, as derived from its behaviour for $T \simeq T_0$. Furthermore, this definition of $C^K$ cannot lead to wrong conclusions at accessible temperatures, provided the value of $ov_0^K$ is also taken to be that given by experiment for $T \simeq T^0$. Other definitions of $C^K$ in the range 0 to $T^0$ can be made to lead to correct results at accessible temperatures by compensating adjustments in the value assumed for $ov_0^K$. In particular one can always assume $C^K$ to behave in the range 0 to $T^0$ in such a manner that the value unity will be found for $ov_0^K$. In case (i) such a procedure would be theoretically correct. In case (ii) it may or may not be true that the modifications in $C^K$, which would appear when the state of true internal equilibrium is substituted for the metastable state, will belong to the range 0 to $T^0$. It is possible they really belong to much higher temperatures. These questions will be discussed in greater detail later in §§ 536–539. We shall first consider the experimental data.

**§ 526. Basis of comparison between theory and experiment.** There are several alternative methods of comparing the theoretical formulae with experiment. The method to be used in each case must depend not only on the kind of experimental data available, but also on our knowledge of the values of the quantities occurring in the theoretical formulae. We shall discuss these methods of comparison in turn.

The molecular mass $m$ is always known, and the moment of inertia $A$ is known from spectroscopic data for most diatomic molecules. The moments of inertia $A, B, C$ for many simple polyatomic molecules are also known from spectroscopic data. The symmetry number $\sigma$ is usually known from the chemical constitution, if not from spectroscopic data. The electronic weight $\varpi_0^G$ of the normal state of the gaseous molecule is also determined spectroscopically for all simple molecules. It is unity for the great majority of

molecules and may safely be assumed unity for all molecules ordinarily called "saturated".

It follows that, at least for simple molecules, one usually has all the data for computing a theoretical value of the chemical constants $j$. But a single chemical constant cannot be compared with experiment; it is only linear combinations of the form

$$\Delta \Sigma j = \Sigma_L l j_L - \Sigma_A a j_A, \tag{526, 1}$$

occurring in formulae such as (510, 17) for $\log K_p$, that can be checked. If the theoretical and experimental values of $\Delta \Sigma j$ agree for a number of reactions involving certain molecular species $A, L, \ldots$, this agreement affords indirect confirmation of the correctness of the theoretical values of the individual chemical constants $j$. In principle this should be the most satisfactory method of testing the theory, provided that a sufficient number of gaseous equilibria could be checked. Unfortunately there are only a few such equilibria, for which sufficiently accurate experimental data are available. Some of these are considered in § 534.

Alternatively one might compare theoretical and experimental values of the vapour pressure constants $i$. This, however, requires a knowledge of theoretical values of $o\upsilon_0^K$ as well as the quantities mentioned above. For this it is necessary to know how the crystals concerned are constructed—that is whether they should be regarded as built up of atomic, molecular (diatomic) or even of multimolecular units. It is safe to assume that when $\upsilon_0^G$ is unity, as it is for the majority of stable molecules, then $\upsilon_0^K$ is also unity. When $\upsilon_0^G$ exceeds unity, we may not assume that $\upsilon_0^K$ is equal to $\upsilon_0^G$. Often the molecules will combine or interact in the crystal to make $\upsilon_0^K$ less than $\upsilon_0^G$, and often equal to unity. To determine the value of $o$ it is further necessary to know whether the molecules can still rotate freely in the crystal at the low limit temperature $T^0$. If they cannot rotate freely it is necessary to know how many distinct orientations are possible with almost equal energy. All these questions will be illustrated by particular examples. It is not yet possible to give the correct answer to these questions *a priori*, but information can be obtained by considering equilibria between solid phases only. According to § 519 a combination of purely calorimetric measurements with either an electromotive force measurement, or a determination of the transition temperature, for a process involving only crystal phases, gives an experimental value for linear combinations of the $\log o\upsilon_0^K$ of the type (519, 4). In § 528 we shall enumerate a number of processes of this type, for which accurate measurements are available. In all these cases the experimental value found for (519, 4) is zero. This can hardly be fortuitous, and suggests that for all the crystals involved $o\upsilon_0^K$ is unity. If $o\upsilon_0^K$ were always unity, there would be, as we have already said, no need to distinguish between the vapour

pressure constants $i$ and the chemical constants $j$. One would then have all the required theoretical data for calculating the vapour pressure constants $i$, and these calculated values could be compared with the experimental. Actually we shall see later that the value of $ov^K$ associated with extrapolation from the values of $T^0$ ordinarily used is probably unity for most, but not all, crystals. We therefore proceed as follows. We compute a theoretical value for the chemical constant $j$, and compare this with the experimental value of the vapour pressure constant $i$. If in most cases we find that these values are equal within the experimental accuracy, this confirms the supposition that for these substances

$$i = j, \quad ov_0^K = 1. \tag{526, 2}$$

In the remaining cases where the calculated value of $j$ and the experimental value of $i$ disagree, we can compute a value of $ov_0^K$ from the relation (518, 1,) and then consider whether, from the chemical structure of the molecule, this value of $ov_0^K$ is explicable by reasonable assumptions about the structure of the crystal.

This method of comparison is convenient for monatomic molecules and also for diatomic molecules, if at ordinary temperatures the rotational degrees of freedom are classical, and the vibrational degrees of freedom either unexcited or at least separable from the rotational. When this is not the case an alternative procedure is adopted. From spectroscopic data one calculates the quantity

$$S^G(T, P) - k \log \Pi\rho, \tag{526, 3}$$

which is obtained by merely omitting the nuclear weights from (523, 2). This is then compared with the experimental value of

$$S^G(T, P) - S^K(0, 0), \tag{526, 4}$$

measured as $\underset{P^\bullet,\, T^\bullet \to 0}{\mathrm{Lt}} \int_{T^\bullet, P^\bullet}^{T,P} dq/T$, the extrapolation from $T = T^0$ to $T = 0$ being performed as described in § 525. The difference obtained by subtracting (4) from (3) is $k \log ov_0^K$, about which information is thus obtained. We shall see that the value so obtained for $\log ov_0^K$ is often but not always zero.

The procedure just described is that adopted by Giauque and his collaborators, and we shall quote numerous examples. The two quantities defined by (3) and (4) are called by Giauque the *spectroscopic entropy* (*nuclear spin omitted*) and the *calorimetric entropy* respectively of the gaseous molecule at the temperature $T$ and pressure $P$. The calculated spectroscopic entropy is the entropy excess over that of an idealized state, in which all the molecules have the same energy, a translational-rotational-vibrational-electronic weight 1, and a nuclear spin weight $\Pi\rho$ equal to the product of the spin weights $\rho$ of the constituent atoms. The measured calorimetric entropy is the entropy excess over the value obtained by smooth extrapolation to $T = 0$ for the crystal. The use of a smooth extrapolation presupposes,

amongst other things, that separation of isotopes does not occur. Correspondingly one ignores the entropy contribution due to the mixing of isotopes in computing the spectroscopic entropy. The conventional nature of any entropy zero used in such calculations has already been emphasized in § 524. If equality is found between the spectroscopic entropy and the calorimetric entropy, it means that smooth extrapolation of the heat capacity leads to a crystal at the absolute zero in which the molecules have a translational-rotational-vibrational-electronic weight unity; in other words $ov_0^K = 1$.

We have seen that the statistical formulae are particularly simple for monatomic gaseous molecules, since these do not involve rotational or vibrational degrees of freedom. It is therefore desirable to obtain as many examples of vapour pressure constants for monatomic gaseous molecules as possible. Experimental values for such constants can in some cases be obtained for monatomic molecules, even when these are not the stable molecules at ordinary temperatures, by combining vapour pressure data for the stable molecule with the data for the dissociation of this molecule into atoms. Thus in the case of a halogen, such as chlorine, one can determine the ordinary vapour pressure due at ordinary temperatures to $Cl_2$ molecules. One can also determine the equilibrium constant between $Cl_2$ molecules and Cl atoms at high temperatures. Then if one knows the heat of dissociation of $Cl_2$ and the heat capacities of $Cl_2$ molecules and Cl atoms, one can calculate the equilibrium constant between $Cl_2$ and Cl at any other temperature. Hence one calculates the immeasurably small pressure of Cl atoms in equilibrium with the diatomic vapour, and therefore with the crystal at low temperatures, and so obtains a value for the vapour pressure constant of monatomic Cl to compare with the theoretical value. It is important to realize that this involves the diatomic molecule only by requiring a knowledge of the heat of dissociation, and of the molecular heat capacity, over the range of temperatures extending from that at which one measures the vapour pressure of $Cl_2$ over the crystal, to that at which one measures the dissociation equilibrium $Cl_2 \rightleftharpoons 2Cl$. In other words we may say that one determines $i_{Cl_2}$ from vapour pressure measurements and

$$(j_{Cl_2} - 2j_{Cl}) = (i_{Cl_2} - 2i_{Cl})$$

from measurements of dissociation equilibria. By combination of these we obtain a value of $i_{Cl}$ to compare with the theoretical value of $j_{Cl}$ and can so determine whether $\log ov_0^K = (i_{Cl} - j_{Cl})$ is zero.

**§ 527. Chemical constants and vapour pressure constants in practical units.** In practice it is customary[A] to use logarithms to base 10 and to measure vapour pressures in atmospheres rather than in dynes/cm.$^2$.

[A] See appendix, § A 3.

If we rewrite our formulae in this manner we obtain new integration constants $j'$, $i'$ defined by

$$j' = \frac{j - \log_e P^\dagger}{\log_e 10}, \tag{527, 1}$$

$$i' = \frac{i - \log_e P^\dagger}{\log_e 10}, \tag{527, 2}$$

where $P^\dagger$ is the value of an atmosphere in dynes/cm.$^2$. These new constants $j'$, $i'$ are conveniently called the *practical chemical constant* and the *practical vapour pressure constant* respectively.

The numerical values of $j'$ are given as follows:

*Monatomic molecules:* $C_P^0/k = \frac{5}{2}$;

$$j' = -1{\cdot}587 + \tfrac{3}{2}\log_{10} M + \log_{10} \upsilon_0^G. \tag{527, 3}$$

*Linear molecules with classical rotations:* $C_P^0/k = \frac{7}{2}$;

$$j' = -3{\cdot}185 + \tfrac{3}{2}\log_{10} M + \log_{10}(10^{40} A) + \log_{10}\frac{\upsilon_0^G}{\sigma}. \tag{527, 4}$$

*Non-linear molecules with classical rotations:* $C_P^0/k = 4$;

$$j' = -3{\cdot}735 + \tfrac{3}{2}\log_{10} M + \tfrac{1}{2}\log_{10}(10^{120} ABC) + \log_{10}\frac{\upsilon_0^G}{\sigma}. \tag{527, 5}$$

In these formulae $M$ is the conventional chemical molecular weight and $A, B, C$ are the three principal moments of inertia of the molecule in gm. cm.$^2$.

The corresponding formulae for $i'$ are given immediately by

$$i' = j' - \log_{10} o\upsilon_0^K. \tag{527, 6}$$

**§ 528. Experimental data for reactions between crystals.** We now consider a physical or chemical process between crystalline phases only. If the heat capacity of each phase has been measured down to temperatures sufficiently low to extrapolate smoothly to $T = 0$ by a formula such as that of Debye, and the heat of reaction has been measured at any one temperature, these data are sufficient to determine the transition temperature, that is the temperature at which the process becomes reversed, provided one knows the value of

$$\Delta\{\Sigma \log o\upsilon_0^K\}. \tag{528, 1}$$

Alternatively from a knowledge of the transition temperature one can calculate the value of (1).

The simplest processes of this type are transitions between two crystalline forms $\alpha$, $\beta$ of a single substance,

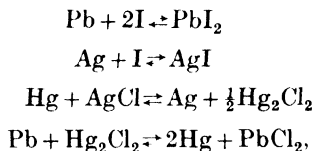
$$\alpha \rightleftharpoons \beta. \tag{528, 2}$$

Experimental study of these tells us the value of

$$\log\{o\upsilon_0^K\}^\alpha - \log\{o\upsilon_0^K\}^\beta. \tag{528, 3}$$

The earlier determinations included the transitions rhombic sulphur to monoclinic sulphur, white tin to grey tin, quartz to cristobalite and calcite to aragonite.* The accuracy was not high, except for the tin transition,† but in all the cases mentioned it is sufficient to exclude a value of (3) numerically as great as $\pm \log 2$. The experimental evidence is therefore in all cases consistent with the supposition $o v_0^K = 1$ for both crystalline forms. The value zero for (3) for the rhombic sulphur to monoclinic sulphur transition has been accurately confirmed by a recent redetermination‡ of the heat capacities of the two forms. The heat capacities of the two solid forms of cyclohexanol§ and of the two solid forms of phosphine‖ have also been determined recently. In both cases the value of (3) is found to be zero with a high degree of accuracy

For the following chemical reactions between crystalline phases,

$$Pb + 2I \rightleftarrows PbI_2$$
$$Ag + I \rightleftarrows AgI$$
$$Hg + AgCl \rightleftarrows Ag + \tfrac{1}{2}Hg_2Cl_2$$
$$Pb + Hg_2Cl_2 \rightleftarrows 2Hg + PbCl_2,$$

there are calorimetric data and electromotive force measurements, from which to evaluate the integration constant. The accuracy is not very high except for the reaction between silver and iodine.¶ In no case does the absolute magnitude found for the integration constant (3) exceed one-third the value of $\log 2$, and the data are consistent, within the experimental accuracy, with the supposition that $o v_0^K$ is unity for each crystalline phase concerned.

## § 529. Experimental vapour pressure data for monatomic molecules.

For monatomic molecules we have always $C_P = C_P^0 = \tfrac{5}{2}k$, and the practical vapour pressure constant is, according to (527, 3) and (527, 6), given by

$$i' = -1{\cdot}587 + \tfrac{3}{2}\log_{10} M + \log_{10} v_0^G/v_0^K. \qquad (529, 1)$$

For a monatomic molecule an orientational factor $o$ other than unity cannot occur. That $o$ is also unity for the halogens is explained below. The experimental data are given in Table 2.

We shall now explain the $v_0^G$ values used. The atoms He, Ne, A, Kr, Xe, Mg, Zn, Cd, Hg in the vapour are in $^1S$ states with a weight $v_0^G = 1$, while Na, K are in $^2S$ states with a weight 2. All other electronic states lie so high that

* *Handb. d. Physik*, **10**, Chapter VII, "Die Bestimmung der freien Energie", by F. Simon. See also Eastman, *Chem. Rev.* **18**, 257 (1936).

† Bronsted, *Zeit Physikal. Chem.* **88**, 479 (1914).

‡ Eastman and McGavock, *J. Am. Chem. Soc.* **59**, 145 (1937).

§ Kelley, *J. Am. Chem. Soc.* **51**, 1400 (1929).

‖ Stephenson and Giauque, *J. Chem. Phys.* **5**, 149 (1937).

¶ Webb, *J. Phys. Chem.* **29**, 816 (1925).

TABLE 2

*Practical vapour pressure constants for monatomic molecules*

$$i' = -1{\cdot}587 + \tfrac{3}{2}\log_{10} M + \log_{10} v_0^g/v_0^K$$

| Formula | Normal electronic state | $v_0^g$ | $j' = i' + \log_{10} v_0^K$ calc. | $i'$ obs. | Authorities for $i'$ observed |
|---|---|---|---|---|---|
| He | $^1S$ | 1 | $-0{\cdot}684$ | $-0{\cdot}68 \pm 0{\cdot}01$ | (14) |
| Ne | $^1S$ | 1 | 0·370 | $0{\cdot}39 \pm 0{\cdot}04$ | (6) |
| A | $^1S$ | 1 | 0·814 | $0{\cdot}81 \pm 0{\cdot}02$ | (10) |
| Kr | $^1S$ | 1 | 1·297 | $1{\cdot}29 \pm 0{\cdot}02$ | (11) |
| Xe | $^1S$ | 1 | 1·590 | $1{\cdot}60 \pm 0{\cdot}02$ | (9) |
| Na | $^2S$ | 2 | 0·757 | $0{\cdot}63 \pm 0{\cdot}03$<br>0·97<br>$0{\cdot}78 \pm 0{\cdot}1$ | (4)<br>(3)<br>(7) |
| K | $^2S$ | 2 | 1·102 | $0{\cdot}92 \pm 0{\cdot}04$<br>1·13 | (4)<br>(3) |
| Mg | $^1S$ | 1 | 0·492 | $0{\cdot}47 \pm 0{\cdot}2$ | (8) |
| Zn | $^1S$ | 1 | 1·136 | $1{\cdot}21 \pm 0{\cdot}15$ | (8) |
| Cd | $^1S$ | 1 | 1·488 | $1{\cdot}45 \pm 0{\cdot}1$<br>1·57 | (2)<br>(5) |
| Hg | $^1S$ | 1 | 1·866 | $1{\cdot}95 \pm 0{\cdot}06$ | (1) |
| Tl | $^2P_{\frac{1}{2}}$ | 2 | 2·180 | $2{\cdot}37 \pm 0{\cdot}3$ | (8) |
| Pb | $^3P_0$ | 1 | 1·888 | $1{\cdot}8 \pm 0{\cdot}2$ | (2), (13) |
| Cl | $^2P_{\frac{3}{2}}$ | * | 1·44 | $1{\cdot}53 \pm 0{\cdot}2$ | (12) |
| Br | $^2P_{\frac{3}{2}}$ | 4 | 1·869 | $2{\cdot}00 \pm 0{\cdot}2$ | (12) |
| I | $^2P_{\frac{3}{2}}$ | 4 | 2·170 | $2{\cdot}19 \pm 0{\cdot}2$ | (12) |

* See Table 3.

*References to Table 2*

(1) Simon, *Zeit. Physikal. Chem.* **107**, 279 (1923).
(2) Egerton, *Proc. Phys. Soc.* **37**, 75 (1925).
(3) Zeidler, *Zeit. Physikal. Chem.* **123**, 383 (1926).
(4) Edmondson and Egerton, *Proc. Roy. Soc.* A, **113**, 533 (1927).
(5) Lange and Simon, *Zeit. Physikal. Chem.* **134**, 374 (1928).
(6) Clusius, *Zeit. Physikal. Chem.* B, **4**, 1 (1929).
(7) Ladenburg and Thiele, *Zeit. Physikal. Chem.* B, **7**, 161 (1930).
(8) Coleman and Egerton, *Phil. Trans.* A, **234**, 177 (1935).
(9) Clusius and Riccoboni, *Zeit. Physikal. Chem.* B, **38**, 81 (1937).
(10) Clusius and Frank, to be published in *Zeit. Physikal. Chem.* B; private communication.
(11) Clusius, Kruis and Konnertz, *Ann. d. Phys.* **33**, 642 (1938).
(12) These values have been obtained as explained in § 526 from the observed values of $2j'_X - j'_{X_2}$ in Table 7 and of $i'_{X_2}$ in Table 4.
(13) The heat of evaporation of liquid Pb is practically independent of temperature throughout the range 1200° K. to 800° K. In the absence of heat capacity data for the range 800° K. to 600° K. the heat of evaporation is assumed to remain unchanged down to the triple point 600° K. Harteck [*Zeit. Physikal. Chem.* **134**, 15 (1928)] by making some alternative, but unexplained, assumption obtains a value 0·4 higher for $i'$.
(14) Simon and Bleaney, *Trans. Far. Soc.* **35**, 1205 (1939).

they do not contribute to the partition function at the relevant temperatures. In Tl vapour the atoms are in a $^2P_{\frac{1}{2}}$ state of weight 2, the upper state $^2P_{\frac{3}{2}}$ of the doublet lying too high to contribute to the partition function. Similarly in Pb vapour the atoms are in a $^3P_0$ state of weight unity, the other states $^3P_1$, $^3P_2$ of the triplet lying too high to contribute to the partition function. For a free halogen atom the normal state is $^2P_{\frac{3}{2}}$ of weight 4, but in this case the other state $^2P_{\frac{1}{2}}$ of weight 2 of the doublet does not lie high enough to be entirely negligible. Hence in place of $\upsilon_0^G = 4$ we must use

$$e(T) = \upsilon_0 + \upsilon_1 e^{-\epsilon_1/kT} = 4 + 2e^{-\epsilon_1/kT}, \qquad (529, 2)$$

where $\epsilon_1$ is the energy difference between the two terms forming the doublet. In Table 3 are given the data for the three halogen atoms Cl, Br, I for the temperatures at which their chemical constants were measured. We see that at these temperatures it is only for Cl that the upper level of the doublet is significant. The calculated $j$ values given in Table 1 were obtained by using $\log_{10} e(T) = 0{\cdot}70$, in place of $\log_{10} \upsilon_0^G = 0{\cdot}60$, for Cl. For Br and I the value $\log_{10} e(T) = \log_{10} \upsilon_0^G = \log_{10} 4 = 0{\cdot}60$ was used.

TABLE 3

*Electronic partition function of free halogen atoms*

$$e(T) = 4 + 2e^{-\epsilon_1/kT}$$

| Atom | $\epsilon_1$ in electron volts | Mean temp. in °K. | $\dfrac{\epsilon_1}{kT}$ | $e(T)$ | $\log_{10} e(T)$ |
|---|---|---|---|---|---|
| Cl | 0·11 | 1000 | 1·28 | 4·56 | 0·66 |
| | | 1700 | 0·752 | 4·94 | 0·69 |
| Br | 0·45 | 1350 | 3·88 | 4·04 | 0·606 |
| I | 0·94 | 1200 | 9·1 | 4·00 | 0·602 |

We see from the table that the values of $j'$ calculated from the known values of $\upsilon_0^G$ agree in all cases within the experimental error with the observed values of $i'$. From this we conclude that in every case $\upsilon_0^K = 1$. We must now consider the physical significance of this. For Ne, A, Kr, Xe, since the crystal is an atomic one, one naturally expects the electronic state to be $^1S$ as in the vapour. For the halogens the crystal structure is one of molecules $Cl_2$, $Br_2$ or $I_2$ in $^1\Sigma$ states. The electronic weight of the normal state of the molecule is therefore unity. The weight of the lowest vibrational state of the crystal regarded as formed of molecules is also unity, and there is no orientational weight $o$ other than unity, when the requirement of antisymmetry in the nuclei is satisfied as explained in § 522.

It remains for us to explain why $\upsilon_0^K$ is unity for the metals including those such as Na, K, Tl for which $\upsilon_0^G$ is not unity. The explanation depends on the

electron theory of metals described in Chapter XI. According to this theory we may regard the atoms in the metal as dissociated into electrons and positive ions, e.g. $Na^+$, $Mg^{++}$, $Tl^+$ (or $Tl^{+++}$); the ions are in a $^1S$ state of weight unity (nuclear weights being as always neglected), and therefore contribute only a factor unity to $v_0^K$. The electrons may be considered to form an electron gas obeying the Fermi-Dirac statistics in an enclosure at nearly constant potential. We shall see in Chapter XI that, at all ordinary temperatures, and *a fortiori* at low temperatures, the N electrons occupy the N states of lowest energy; this distribution corresponds to a single eigen function for the assembly. Thus $v_0^K$ remains unity in agreement with experiment.

**§ 530. Experimental vapour pressure data for diatomic molecules other than hydrogen and deuterium.** For all diatomic molecules, except $H_2$, HD, $D_2$ which are considered separately in the following section, the rotational degrees of freedom are at least approximately classical, and separable from the vibrational degrees of freedom. According to (525, 1) the rotational partition function, at temperatures where the rotations do not deviate greatly from their classical behaviour, is given by

$$\log r(T) = \log\frac{T}{\Theta_r}+\frac{1}{3}\frac{\Theta_r}{T} = \log\frac{8\pi^2 AkT}{h^2}+\frac{1}{3}\frac{39\cdot 6}{(10^{40}A)\,T}, \qquad (530, 1)$$

the second term representing the deviation from completely classical behaviour. Taking HCl as an example of a diatomic molecule with a small moment of inertia, we have $A = 2\cdot 66\times 10^{-40}$ g. cm.$^2$. Inserting this value into (1) we find that the deviation of $\log r(T)$ from its classical value is only 0·016 at 300° K. This will introduce an error[A] of 0·016 into $\iota$ or of 0·007 into $\iota'$. This corresponds to an error of nearly 2 % in the calculated vapour pressure, but is less than the error due to experimental uncertainties in the heat capacity of the solid.* For most other molecules, except $H_2$, HD, $D_2$, the situation is more favourable. Thus for $N_2$ we have $A = 13\cdot 8\times 10^{-40}$ g. cm$^{2}$. Hence the deviations will be about five times smaller at 300° K. and will have the above values at about 60° K. We may therefore, for most molecules at most temperatures, set $C_P^0 = \frac{7}{2}k$, and use (527, 4) for the practical chemical constant to which the vapour pressure constant is related by (527, 6).

* It is worth noting that the corresponding corrections to the molecular energy $E$, heat function $H$, free energy $F$ and Gibbs' function $G$ are (for not too low temperatures) independent of the temperature and have the value $\frac{1}{3}h^2/8\pi^2A$ per molecule, which is one-sixth the energy separation of the first and zeroth rotational states. This deviation thus amounts to $13\cdot 2/10^{40}A$ calories For HCl this is 5 cal /mole. For $H_2$ it is 28 5 cal mole. The analogous correction to the translational energy is completely insignificant

[A] See appendix, § A4.

A comparison between theory and experiment is given in Table 4. From the known values of $A$ and $\upsilon_0^G$, obtained from spectroscopic data, one calculates $j'$, and this is compared with the experimental value for $i'$. The difference between these should be equal to $\log_{10} o\upsilon_0^K$. In most but not all cases the data indicate that $o\upsilon_0^K$ is unity. We shall now discuss the $o\upsilon_0^K$ values individually. We postpone discussion of $H_2$, HD and $D_2$ to § 531.

Nitrogen is typical of a symmetrical molecule in a $^1\Sigma$ state, so that $\upsilon_0^G = 1$ and we may safely assume that $\upsilon_0^K = 1$ also. All such molecules other than $H_2$, HD, $D_2$ have ceased rotating at comparatively high temperatures, and the extrapolation of $C^K$ proceeds from a temperature $T^0$ at which the molecule is free only to oscillate about a direction of equilibrium. If this direction is unique, there will not be more than one distinguishable equilibrium position for the molecule and $o$ will be unity. We then have $o\upsilon_0^K = 1$ in agreement with the facts.

For mixtures of isotopes such as chlorine there are two types of molecules; the symmetrical such as $^{35}Cl\,^{35}Cl$ and the unsymmetrical such as $^{35}Cl\,^{37}Cl$. For the former the symmetry number $\sigma = 2$, and as for $N_2$ we may expect $\upsilon_0^K = 1, o = 1$. For the latter $\sigma = 1$, but now $o = 2$ because of the two distinct equilibrium directions of orientation of the molecule in the crystal. Hence as explained in § 511 and § 521 we may for convenience obtain correct results* by ignoring the small degree of asymmetry and use a fictitious $\sigma = 2, o = 1$ for $^{35}Cl\,^{37}Cl$ the same as for $^{35}Cl\,^{35}Cl$.

The molecules HCl, HBr, HI are typical of unsymmetrical molecules in a $^1\Sigma$ state. For these $\upsilon_0^G = 1$ and so presumably $\upsilon_0^K = 1$. As these molecules have an electric moment, they can have only one unique direction of equilibrium in the crystal at low temperatures, and $o = 1$. Hence $o\upsilon_0^K = 1$ in agreement with the data.

CO is one of the few examples where the data seem to indicate that $o\upsilon_0^K \neq 1$. As the normal electronic state is $^1\Sigma$, we have $\upsilon_0^G = 1$ and so presumably also $\upsilon_0^K = 1$. It has been suggested† that the CO molecules have such a small electric moment and are so nearly symmetrical, that in the crystal there is randomness between the two opposite directions of orientation down to the lowest temperatures at which measurements have been made. If this is the case, then $o = 2$ and the agreement between the calculated and observed values of $i'$ becomes reasonably good.

We have still to consider the two molecules not in $^1\Sigma$ states. The gaseous $O_2$ is in a $^3\Sigma$ state with weight 3, and one might have expected this weight to persist in the crystal. Actually the data indicate that $o\upsilon_0^K$ is unity. This would required the $O_2$ molecules in the crystal to be lined up with their

* Compare Giauque and Overstreet, *J. Am. Chem. Soc.* **54**, 1731 (1932).

† Clayton and Giauque, *J. Am. Chem. Soc.* **54**, 2610 (1932).

TABLE 4

*Practical vapour pressure constants for diatomic molecules*

$$i' = j' - \log_{10} ov_0^K = -3{\cdot}185 + \tfrac{3}{2}\log_{10} M + \log_{10} 10^{40}A + \log_{10}\frac{v_0^G}{\sigma ov_0^K}$$

| Formula | $A \times 10^{40}$ g. cm.$^2$ | Normal electronic state | $v_0^G$ | Symmetry number $\sigma$ | $j'$ calc. | $i'$ calc. | $i'$ obs. | $ov_0^K$ |
|---|---|---|---|---|---|---|---|---|
| $H_2$ ($T > 300$) | 0·463 | $^1\Sigma$ | 1 | 2 | −3·37 | — | — | 3[illegible] |
| $D_2$ ($T > 300$) | 0·931 | $^1\Sigma$ | 1 | 2 | −2·61 | — | — | 3[illegible] |
| HD ($T > 300$) | 0·621 | $^1\Sigma$ | 1 | 1 | −2·68 | — | — | 1 |
| $N_2$ | 13·8 | $^1\Sigma$ | 1 | 2 | −0·175 | −0·175 | −0·16 ± 0·03 | 1 |
| $O_2$ | 19·1 | $^3\Sigma$ | 3 | 2 | 0·53 | 0·53 | 0·55 ± 0·02 | 1 |
| NO ($T \simeq 120$) | 16 4 ($^2\Pi_{\frac{1}{2}}$) | $^2\Pi_{\frac{1}{2}}, ^2\Pi_{\frac{3}{2}}$ | $2(1+e^{-178/T})$ | 1 | 0·63 | 0·48 | 0·55 ± 0·03 | 2[illegible] |
| ($T \gg 178$) | 16 0 ($^2\Pi_{\frac{3}{2}}$) | $^2\Pi$ | 4 | 1 | 0·84 | 0·69 | — | 2[illegible] |
| CO | 14 3 | $^1\Sigma$ | 1 | 1 | 0·14 | −0·16 | −0·07 ± 0·05 | 2 |
| HCl | 2 61 | $^1\Sigma$ | 1 | 1 | −0·42 | −0·42 | −0·40 ± 0·03 | 1 |
| HBr | 3·27 | $^1\Sigma$ | 1 | 1 | 0·19 | 0·19 | 0·24 ± 0·04 | 1 |
| HI | 4·40 | $^1\Sigma$ | 1 | 1 | 0·62 | 0·62 | 0·65 ± 0·05 | 1 |
| $Cl_2$ | 113 | $^1\Sigma$ | 1 | 2 | 1·35 | 1·35 | 1·66 ± 0·08 | 1 |
| $Br_2$ | 342 | $^1\Sigma$ | 1 | 2 | 2 35 | 2·35 | 2·59 ± 0·10 | 1 |
| $I_2$ | 742 | $^1\Sigma$ | 1 | 2 | 2·99 | 2·99 | 3·08 ± 0·05 | 1 |

Experimental values are taken from Eucken, *Physikal. Zeit.* **31**, 361 (1930).

nuclear spins oriented in a unique regular manner.* An alternative possibility is the formation of $O_4$ molecules with a weight unity. We should therefore expect crystalline oxygen to become diamagnetic at extremely low temperatures. The experimental evidence is discussed by Giauque and Johnston but it is inconclusive.

The normal electronic state of NO is $^2\Pi_{\frac{1}{2}}$, but the other state $^2\Pi_{\frac{3}{2}}$ of the doublet is not much higher. As explained in § 325 we therefore take the electronic partition function as given by

$$e(T) = 2 + 2e^{-\epsilon_1/kT} = 2(1 + e^{-178/T}).$$

This expression must be used in place of $\varpi_0^G$ in the formula for the vapour pressure constant. At the boiling-point $T' = 121{\cdot}4°$ K. we have $e(T) = 2{\cdot}28$, and this value must be used in place of $\varpi_0^G$ for comparison with experiment in the neighbourhood of this temperature. At $T = 300°$ K. we have $e(T) = 3{\cdot}10$, whilst when $T \gg 178°$ K. we have $e(T) = 4$, the two energy levels of the doublet behaving effectively as a single energy level. It is this last value for $e(T)$ that has to be used in § 534, where the high temperature equilibrium between $N_2$, $O_2$ and NO is considered. When the chemical constant $j'$ thus calculated is compared with the observed vapour pressure constant $i'$ in the neighbourhood of $T = 120°$ K., it is found that there is a discrepancy. This has been interpreted by Johnston and Giauque† as due to a crystal of $N_2O_2$ molecules, each in a state of weight 2. This would give a statistical weight for the lowest energy level in the crystal of 2 per $N_2O_2$ or $2^{\frac{1}{2}}$ per NO. The discrepancy between $j'$ calculated and $i'$ observed is in good agreement with the supposition that $o\varpi_0^K = 2^{\frac{1}{2}}$. The weight 2 per $N_2O_2$ molecule is what one would expect if the molecules have the shape $\begin{smallmatrix}\mathrm{NO}\\\mathrm{ON}\end{smallmatrix}$, since owing to the similarity of N and O atoms the two orientations $\begin{smallmatrix}\mathrm{NO}\\\mathrm{ON}\end{smallmatrix}$ and $\begin{smallmatrix}\mathrm{ON}\\\mathrm{NO}\end{smallmatrix}$ would presumably have effectively equal energies.

**§ 531. The special cases of hydrogen and deuterium.** We have still to consider hydrogen and deuterium, as these molecules present special features meriting careful consideration. The moment of inertia of $H_2$ is only $0{\cdot}463 \times 10^{-40}$ g. cm.² so that

$$\Theta_r = \frac{h^2}{8\pi^2 Ak} = \frac{39{\cdot}6}{10^{40}A} = 85{\cdot}4 \text{ deg.} \qquad (531, 1)$$

Thus according to (530, 1) the deviation of $\log r(T)$ from its classical value at 300° K. will be $\frac{1}{3}\Theta_r/300 = 85{\cdot}4/900 = 0{\cdot}095$. The corresponding correction

* Giauque and Johnston, *J. Am. Chem. Soc.* **51**, 2300 (1929).
† Johnston and Giauque, *J. Am. Chem. Soc.* **51**, 3194 (1929).

in $j$ is 0·095 and that in $j'$ is 0·041, which is comparable with the experimental uncertainty. Thus in the case of $H_2$ the classical approximation for $r(T)$ may be just allowable at temperatures above 300° K., but is certainly not allowable at lower temperatures. It may be emphasized that the deviation of $\log r(T)$, and so of $j$, from its classical value may well be appreciable even though deviations of $C_P/k$ from its classical value $\frac{7}{2}$ are inappreciable. For the rotational contribution to the heat capacity of a diatomic molecule is, according to (313, 6), given by

$$\frac{C^{\mathrm{rot}}}{k} = 1 + \frac{1}{45}\left(\frac{\Theta_r}{T}\right)^2 = 1 + \frac{1}{45}\left(\frac{h^2}{8\pi^2 A\,kT}\right)^2 = 1 + \frac{1}{45}\left(\frac{39\cdot 6}{10^{40} A\,T}\right)^2. \quad (531, 2)$$

For $H_2$ at 300° K. this gives $C^{\mathrm{rot}}/k = 1\cdot 002$, thus differing insensibly from unity. On the other hand the error in $j'$, computed above as 0·042, corresponds to an error of no less than 10 % in the partial pressure of the gas. For $D_2$ the error in $j'$ is about half as great as for $H_2$ at the same temperature.

For the molecules $H_2$, HD and $D_2$ we may therefore use the usual formulae for the chemical constant $j$ of a diatomic molecule only at temperatures above 300° K. We may further continue to use such formulae at slightly lower temperatures if we add a correction term $\frac{1}{3}\Theta_r/T \log_e 10$ to the value of $j'$ calculated by assuming classical rotations. All temperatures at which this procedure is allowable are considerably higher than the critical temperature 33° K., and one has then no use for a vapour pressure constant $i$. Experimental evidence for the correctness of the values of $j'$ thus calculated for high temperatures is afforded by the equilibrium data for reactions involving hydrogen or deuterium. Such reactions are included in Table 7.

At lower temperatures when the condition $T \gg \Theta_r$ fails, we have to use an entirely different method for taking account of the properties of $H_2$, $D_2$, HD. In particular, as we saw in Chapter III, we have to treat $H_2$ as a mixture of two non-interconvertible species $p$-$H_2$ and $o$-$H_2$. This also applies to $D_2$, but not to HD. Not only does the classical condition $T \gg \Theta_r$ fail for hydrogen, except for temperatures above 300° K., but it is comparatively easy to reach temperatures at which the opposite condition $T \ll \Theta_r$ holds. At such temperatures the rotations will be effectively unexcited. In the case of $p$-$H_2$ the normal rotational state, of quantum number 0, has weight 1 and the first excited state, of rotational quantum number 2, has weight 5 and energy $6k\Theta_r$. The ratio of the number of $p$-$H_2$ molecules in the rotational state 2 to the number in the rotational state 0 is therefore $5e^{-6\Theta_r/T} : 1$. At the temperature $T = 43°$ K., corresponding to $\Theta_r/T = 2$, this fraction is only $3 \times 10^{-5}$. For $o$-$H_2$ the ratio of the number of molecules in the state of rotational quantum number 3 to the number in the ground state of rotational quantum number 1 is similarly $7e^{-12\Theta_r/T} : 3e^{-2\Theta_r/T}$. At $T = 43°$ K. this fraction is

only $5 \times 10^{-9}$. Thus at this temperature the fraction of $H_2$ molecules, whether para or ortho, not in the lowest accessible rotational state is entirely negligible. This is equally true of $D_2$ at temperatures half as great as for $H_2$.

To obtain formulae for $H_2$, $D_2$ and HD at all temperatures appreciably less than room temperature we use the procedure described in § 525. We take $C_P^0 = \frac{5}{2}$ and define $C'(T)$ by

$$C'(T) = C_P - \tfrac{5}{2}k \quad (T > T^0),$$
$$C'(T) = 0 \qquad (T < T^0), \tag{531, 3}$$

where $T^0$ is a temperature in the range where the rotational degrees of freedom are unexcited. For $H_2$ we can take $T^0$ as any temperature say between 20° and 40°. With these definitions of $C_P^0$ and $C'(T)$, it follows from (510, 14) that, for any temperature $T > T^0$ (say $T > 20°$ K.),

$$\frac{\mu}{kT} = \frac{H^0}{kT} + \log p - \tfrac{5}{2}\log T - \int_{T^0}^{T} \frac{dT_1}{T_1^2}\int_{T^0}^{T_1} \frac{C'(T_2)}{k} dT_2 - j_0; \tag{531, 4}$$

the integration constant $j_0$ can be determined as follows. The term in (4) containing $C'(T)$ is equal to $-\log\{r_n(T)/r_n(T^0)\}$, while the rotational-nuclear contribution to $\mu/kT$ is $-\log r_n(T)$. Thus the rotational-nuclear term in $j_0$ has to be $\log r_n(T^0)$. The remaining terms in $j_0$ are contributions from the translational and electronic degrees of freedom, which have their usual forms. We therefore have

$$j_0 = \log\frac{(2\pi m)^{\frac{3}{2}} k^{\frac{5}{2}}}{h^3} - v_0 + \log r_n(T^0). \tag{531, 5}$$

Before discussing the value of $r_n(T^0)$ we shall consider the behaviour of the crystal.

Owing to their small moments of inertia and their nearly spherical external field of force, the molecules $H_2$, $D_2$ and HD continue to rotate in the crystal down to temperatures as low as 12° K. These rotations are of course not classical, and below about 40° K. only the rotational states of least quantum number consistent with the symmetry of the para or ortho form are occupied. At still lower temperatures an orientational interaction between the molecules will remove the triple degeneracy of the lowest rotational state of ortho-hydrogen. This should show itself by an extra contribution to the heat capacity superposed on the contribution of the lattice vibrations, which has in fact been observed* at temperatures below 12° K., and is shown in Fig. 1. It should be noticed that the extra heat capacity increases with the relative amount of ortho-hydrogen, and vanishes for pure para-hydrogen, because the lowest rotational state of the latter is not degenerate. It is still customary to evaluate the integral containing

* Mendelssohn, Ruhemann and Simon, *Zeit. Physikal. Chem.* B, **15**, 121 (1931).

$C'(T)$ by smooth extrapolation from above 12° K, since sufficiently complete data are not yet available for any other choice of $T^0$. When we use this method of extrapolation, the orientational weight $o$ associated with it is not unity for either $H_2$ or $D_2$ owing to the ortho para metastability, but is unity for HD.

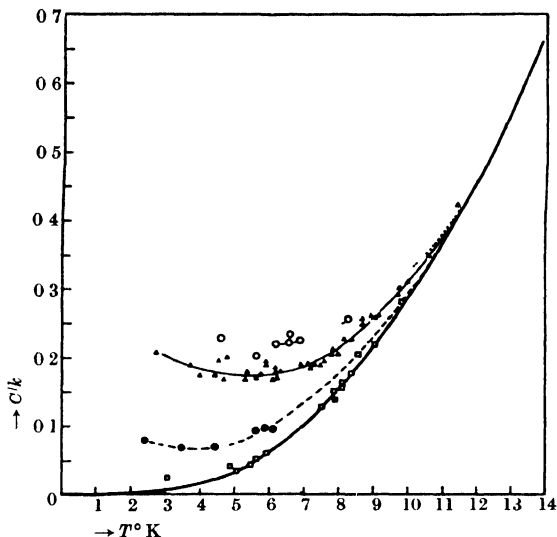



Fig 1 Heat capacity of solid hydrogen

——— Pure para ----- 75% para, 25% ortho

——— 50% para, 50% ortho 25% para, 75% ortho

For $H_2$ the para molecules have a least rotational quantum number 0 and weight 1, and the ortho molecules have a least rotational quantum number 1 and weight 3. We also recall that ordinary $H_2$ is a mixture of 1 part para to 3 parts ortho. We thus have for the value of the orientational factor $o$ in the crystal

$$\log o = \log 1 = 0 \quad (p\ H_2), \tag{531, 6}$$

$$\log o = \log 3 \quad (o\ H_2) \tag{531, 7}$$

The nuclear spin weights to be used with these values of $o$ are 1 and 3 respectively. To derive the value of $o$ for the ordinary metastable mixture of para- and ortho hydrogen, we make use of the principle, established in § 522, that for the ordinary mixture we obtain correct results by ignoring differences between the nuclear weights of the para and ortho forms, provided we also ignore the factor due to mixing. We thus obtain

$$\log o = \tfrac{1}{4}\log 1 + \tfrac{3}{4}\log 3 = \tfrac{3}{4}\log 3 \quad (\text{ordinary } H_2), \tag{531, 8}$$

the associated nuclear spin weight being $2^2$. For the more general example

of a mixture of $1-x$ parts of para- and $x$ parts of ortho-hydrogen we cannot use any such short cut. For such a mixture we obtain for the limiting value of the partition function $f(0)$ per molecule in the crystal, taking account of the mixing factor as well as the nuclear and rotational factors, and assuming the electronic weight to be unity,

$$\log f(0) = \{(1-x)\log 1 + x\log 9\} - \{(1-x)\log(1-x) + x\log x\}$$

$$= (1-x)\log\left(\frac{1}{1-x}\right) + x\log\left(\frac{9}{x}\right). \qquad (531,9)$$

For the special case $x = \frac{3}{4}$ this reduces, in agreement with (8), to

$$\log f(0) = \tfrac{3}{4}\log 3 + \log 4 = \log o + \log \rho^2. \qquad (531,10)$$

For $D_2$ it is the ortho molecules (with nuclear spin weight 6) that have a lowest rotational state of quantum number 0 and weight 1, and the para molecules (with nuclear spin weight 3) that have a lowest rotational state of quantum number 1 and weight 3. The proportion of ortho to para molecules in the ordinary metastable mixture is equal to the ratio of the nuclear spin weights, namely 6 : 3. Hence the values of $o$ are given by

$$\log o = \log 1 = 0 \quad (o\text{-}D_2), \qquad (531,11)$$

$$\log o = \log 3 \quad (p\text{-}D_2), \qquad (531,12)$$

$$\log o = \tfrac{6}{9}\log 1 + \tfrac{3}{9}\log 3 = \tfrac{1}{3}\log 3 \quad (\text{ordinary } D_2). \qquad (531,13)$$

For HD, since there are no para and ortho forms, all the molecules will at low temperatures be in the lowest rotational state of weight 1, and we have simply $o = 1$.

We can now combine the results obtained for the crystal with formula (5) for the gas to obtain the vapour pressure of a mixed crystal of para and ortho forms in any proportions, provided that we neglect any difference between the proportions in the two phases. For at the temperature $T^0$ (between 12° and 40°) it is true both in the gas and in the crystal that every molecule, whether para or ortho, will be in its lowest accessible rotational state Thus in taking the difference of partial potentials, or the ratio of the partition functions, between crystal and vapour all contributions of rotations, nuclear spins and mixing will cancel. In fact the value of $r_n(T^0)$ in the gas, averaged according to the proportions of para and ortho, is precisely equal to the value of $o\rho_a\rho_b$ in the crystal obtained by similar averaging. We thus have the simple result, valid equally for $H_2$, $D_2$ and HD and for any ratio of para to ortho forms,

$$i = \log\left\{\frac{(2\pi m)^{\frac{3}{2}} k^{\frac{5}{2}}}{h^3} \frac{v_0^G}{v_0^K}\right\} \quad (C_P^0 = \tfrac{5}{2}k), \qquad (531,14)$$

of precisely the same form as for monatomic molecules. Since all these

molecules are in $^1\Sigma$ states the electronic weights $\upsilon_0^G$ and $\upsilon_0^K$ are unity and may be omitted.

The value of $i'$ thus calculated for $H_2$ is $-1{\cdot}13$ as compared with the observed value* $-1{\cdot}09 \pm 0{\cdot}02$. For $D_2$ the calculated value of $i'$ is $-0{\cdot}68$ in excellent agreement with the experimental‡ value $-0{\cdot}67$.

The experimental data for HD are incomplete, since the heat capacities of crystalline and liquid HD have not been measured. It so happens, however, that the experimental heat capacities of condensed $H_2$ and $D_2$ are almost identical over the whole experimental temperature range. This equality is presumably accidental. If then one makes the plausible assumption§ that the heat capacity of condensed HD is at all temperatures equal to those of $H_2$ and $D_2$, one can compute an experimental value of $i'$. The value so calculated exceeds the theoretical value by only $0{\cdot}02$, which is within the experimental error.

**§ 532. Comparison of calorimetric and spectroscopic data for diatomic molecules.** When the available calorimetric and spectroscopic data are sufficiently accurate, it may be convenient to compare, as described in §§ 523 and 526,

$$S^G(T, P) - S^K(0, 0), \qquad (532, 1)$$

determined calorimetrically, with

$$S^G(T, P) - k\Sigma \log \rho \qquad (532, 2)$$

determined spectroscopically. When (1) is subtracted from (2) one obtains

$$k \log o\upsilon_0^K. \qquad (532, 3)$$

This is essentially the procedure adopted by Giauque and his collaborators, who call (1) the "calorimetric entropy" and (2) the "spectroscopic entropy (without nuclear spin)" per molecule of gas at the temperature $T$ and pressure $P$.

To evaluate the "spectroscopic entropy" for one mole we insert numerical values into (523, 2) and obtain

$$\mathbf{N}S^G(T, P) - R\Sigma \log \rho = -R \log \frac{P}{P^\dagger} + \tfrac{5}{2}R \log T + R \log r\upsilon(T) + R\frac{\partial \log r\upsilon(T)}{\partial T}$$
$$+ \tfrac{3}{2}R \log M - R \log \sigma - 2{\cdot}300 \text{ cal./deg. mole}, \qquad (532, 4)$$

where $P^\dagger$ is one atmosphere measured in the same units as $P$ ($P/P^\dagger$ is thus the value of the pressure in atmospheres), and $M$ is the conventional chemical molecular weight. When it is allowable to separate the rotational

* Eucken, Karwat and Fried, *Zeit Phys* **29**, 1 (1924).
‡ Clusius and Bartholomé, *Zeit. Physikal Chem* B, **30**, 258 (1935)
§ See Clusius, Popp and Frank, *Physica*, **4** (no 10), 1113 (1937).

degrees of freedom from the vibrational, and to treat the former as classical, we may replace (4) by

$$\mathsf{N}S^G(T, P) - R\Sigma \log \rho = -R\log\frac{P}{P\dagger} + \tfrac{7}{2}R\log T + R\log q(T) + R\frac{\partial \log q(T)}{\partial T}$$
$$+ \tfrac{3}{2}R\log M + R\log(10^{40}A) - R\log\sigma - 7{\cdot}62 \text{ cal./deg. mole}, \quad (532, 5)$$

where $A$ is the principal moment of inertia in g. cm.$^2$.*

Giauque does not use the approximation (5) but calculates the "spectroscopic entropy" from (4). In Table 5 we give a list of the data for diatomic molecules obtained in this way, mostly by Giauque and his collaborators. This comparison between theory and experiment, though in principle equivalent to that of the preceding section, is more accurate for two reasons.

TABLE 5

*Molar entropy of diatomic gases at* 298·1° K. *and* 1 *atmosphere*

| Substance | "Calorimetric entropy" observed cal./mole deg. | "Spectroscopic entropy" cal./mole deg. | $ov_0^{\pi}$ assumed | "Calorimetric entropy" calculated cal./mole deg. | References |
|---|---|---|---|---|---|
| $H_2$ | 29·7 | 31·23 | $3^{3/4}$ | 29·59 | (1) |
| $D_2$ | 33·9 | 34·62 | $3^{1/3}$ | 33·90 | (2) |
| $N_2$ | 45·9 | 45·79 | 1 | 45·79 | (3) |
| $O_2$ | 49·1 | 49·03 | 1 | 49·03 | (4) |
| HCl | 44·5 | 44·64 | 1 | 44·66 | (5), (7), (10) |
| HBr | 47·6 | 47·48 | 1 | 47·48 | (6), (7) |
| HI | 49·5 | 49·4 | 1 | 49·4 | (7) |
| CO | 46·2 | 47·32 | 2 | 45·93 | (8) |
| NO‡ | 43·0 | 43·75 | $2^{1/2}$ | 43·06 | (9) |

‡ In the case of NO the data refer to 121·36° K., for all other substances to 298·1° K.

*References to Table* 5

(1) Giauque, *J. Am. Chem. Soc.* **52**, 4816 (1930); Giauque and Johnston, *Phys. Rev.* **36**, 1592 (1930).
(2) Clusius and Bartholomé, *Zeit. Physikal. Chem.* B, **30**, 258 (1935).
(3) Giauque and Clayton, *J. Am. Chem. Soc.* **55**, 4875 (1933).
(4) Giauque and Johnston, *J. Am. Chem. Soc.* **51**, 2300 (1929).
(5) Giauque and Wiebe, *J. Am. Chem. Soc.* **50**, 101 (1928).
(6) Giauque and Wiebe, *J. Am. Chem. Soc.* **50**, 2193 (1928).
(7) Giauque and Wiebe, *J. Am. Chem. Soc.* **51**, 1441 (1929).
(8) Clayton and Giauque, *J. Am. Chem. Soc.* **54**, 2610 (1932); Giauque and Clayton, *J. Am. Chem. Soc.* **55**, 5071 (1933).
(9) Johnston and Giauque, *J. Am. Chem. Soc.* **51**, 3194 (1929).
(10) Giauque and Overstreet, *J. Am. Chem. Soc.* **54**, 1731 (1932).

* It is inadvisable to include the term $R\log 10^{40}$ in the numerical constant, because the value of this term is sensitive to the exact value assigned to $R$. Thus an error of 0·001 cal./deg. in $R$ will give an error of 0·09 cal./deg. in $R\log 10^{40}$, but this will cancel the corresponding error in $R\log A$, provided the same value of $R$ is used consistently. If we assume $R = 1{\cdot}9864$ cal./deg., then $R\log 10^{40} - 7{\cdot}62 = 182{\cdot}96 - 7{\cdot}62 = 175{\cdot}34$. Clusius uses the value $175{\cdot}30_5$.

Firstly most of the experimental data in Table 4 are older than those of Giauque, and considerably less accurate. [The data for the hydrogen halides are the same in both tables.] Most of Giauque's data are accurate to at least 0·1 cal./mole deg. Secondly the calculations, being based on the spectroscopically determined energy levels, are independent of any approximations concerning the rotational-vibrational motion. The probable significance of the values of $ov_0^K$ has already been discussed in the preceding sections.

When the gas is not completely perfect the observed "calorimetric entropy" has been corrected to the value it would have were the gas perfect. The correction is given by the thermodynamic formula

$$S^{\text{ideal}} - S^{\text{actual}} = \int_{P^*}^{P} dP\left\{\left(\frac{\partial S}{\partial P}\right)_T^{\text{ideal}} - \left(\frac{\partial S}{\partial P}\right)_T^{\text{actual}}\right\}$$
$$= \int_{P^*}^{P} dP\left\{\left(\frac{\partial V}{\partial T}\right)_P^{\text{actual}} - \left(\frac{\partial V}{\partial T}\right)_P^{\text{ideal}}\right\}, \qquad (532, 6)$$

where $P^*$ is any pressure sufficiently low for the gas to be ideal. If the $(P, V, T)$-relation for the gas is known, this correction is easily calculated. It is always small, usually not exceeding 0·3 cal./mole deg.

**§ 533. Comparison of calorimetric and spectroscopic data for polyatomic molecules.** We turn now to polyatomic molecules. Formulae (531, 1) to (532, 4) apply to polyatomic as well as to diatomic molecules. When it is allowable to separate the rotational degrees of freedom from the vibrational, and to treat the former as classical, we may replace (532, 4) by‡

$$\mathbf{N}S^G(T, P) - R\Sigma \log \rho = -R\log\frac{P}{P\dagger} + 4R\log T + R\Sigma_v \log q_v(T)$$
$$+ R\Sigma_v \frac{\partial \log q_v(T)}{\partial T} + \tfrac{3}{2}R\log M + \tfrac{1}{2}\log(10^{120}ABC)$$
$$- R\log\sigma - 9{\cdot}14 \text{ cal./deg. mole}, \qquad (533, 1)$$

valid for non-linear molecules. For linear polyatomic molecules we have merely to use (532, 5) with each term in $q(T)$ replaced by a sum of several similar terms in $q_v(T)$ for the several normal modes.

We shall now discuss those polyatomic molecules for which both accurate calorimetric data and reliable spectroscopic data are available.§

The data are given in Table 6, where we have again used Giauque's nomenclature, namely "calorimetric entropy" for (532, 1) and "spectroscopic entropy" for (532, 2). The values of the former are corrected from actual gas

‡ If we assume $R = 1{\cdot}9864$ cal./deg., then $R\log_e 10^{60} - 9{\cdot}14 = 274{\cdot}44 - 9{\cdot}14 = 265{\cdot}30$. Clusius uses the value 265·44 and Giauque the value 265·35. Compare footnote, p. 211.

§ A useful survey of the data previous to 1936 has been compiled by Kassel, *Chem. Rev.* **18**, 277 (1936).

TABLE 6

*Molar entropies of polyatomic gases at their boiling-points at 1 atmosphere*

| Substance | Symmetry number $\sigma$ | Boiling-point °K. | "Calorimetric entropy" observed cal./deg. mole | "Spectroscopic entropy" cal. deg. mole | $\sigma v_0^K = o$ assumed | "Calorimetric entropy" calculated cal./deg. mole | References |
|---|---|---|---|---|---|---|---|
| $OH_2$ | 2 | * | 44·28 | 45·10 | $\frac{3}{2}$ | 44·29 | (1) |
| $OD_2$ | 2 | * | 45·89 | 46·66 | $\frac{3}{2}$ | 45·85 | (2) |
| $SH_2$ | 2 | 212·77 | 46·38 | 46·44 | 1 | 46·44 | (3) |
| | | 212·8 | 46·33 | 46·42 | 1 | 46·42 | (4) |
| $NH_3$ | 3 | 239·68 | 44·13 | 44·10 | 1 | 44·10 | (5) |
| $PH_3$ | 3 | 185·38 | 46·39 | 46·5 ± 1·0 | 1 | 46·5 ± 1·0 | (6) |
| | | 185·7 | 46·39 | 46·4 | 1 | 46·4 | (7) |
| $CH_4$ | 12 | 111·5 | 36·53 | 36·61 | 1 | 36·62 | (8) |
| $CH_3D$ | 3 | 99·7 | 36·72 | 39·49 | 4 | 36·73 | (9) |
| $CO_2$ | 2 | 194·67 | 47·59 | 47·55 | 1 | 47·55 | (10) |
| NNO | 1 | 184·59 | 47·36 | 48·50 | 2 | 47·12 | (11) |
| $CS_2$ | 2 | 318·39 | 57·48 | 57·60 | 1 | 57·60 | (12) |
| SCO | 1 | 222·87 | 52·56 | 52·66 | 1 | 52·66 | (13) |
| $SO_2$ | 2 | 263·08 | 58·07 | 58·23 ± 0·15 | 1 | 58·23 ± 0·15 | (14) |
| $C_2H_4$ | 4 | 169·4 | 47·36 | 47·35 | 1 | 47·35 | (15) |
| $CH_3Br$ | 3 | 276·66 | 57·86 | 57·99 | 1 | 57·99 | (16) |

* The values given for $OH_2$ and $OD_2$ are for 298·1° K., and not for the boiling-point.

*References to Table 6*


(1) Giauque and Stout, *J. Am. Chem Soc* **58**, 1144 (1936).
(2) Long and Kemp, *J. Am. Chem. Soc* **58**, 1829 (1936).
(3) Giauque and Blue, *J. Am. Chem. Soc* **58**, 831 (1936).
(4) Clusius and Frank, *Zeit. Physikal. Chem.* B, **34**, 420 (1936).
(5) Overstreet and Giauque, *J. Am. Chem. Soc.* **59**, 254 (1937).
(6) Stephenson and Giauque, *J. Chem. Phys.* **5**, 149 (1937).
(7) Clusius and Frank, *Zeit. Physikal. Chem.* B, **34**, 405 (1936).
(8) Frank and Clusius, *Zeit. Physikal. Chem.* B, **36**, 291 (1937).
(9) Clusius, Popp and Frank, *Physica*, **4** (no. 10), 1105 (1937).
(10) Giauque and Egan, *J. Chem Phys.* **5**, 45 (1937).
(11) Blue and Giauque, *J. Am. Chem. Soc.* **57**, 991 (1935).
(12) Brown and Manov, *J. Am. Chem. Soc.* **59**, 500 (1937).
(13) Kemp and Giauque, *J. Am. Chem. Soc.* **59**, 79 (1937).
(14) Giauque and Stephenson, *J. Am. Chem. Soc.* **60**, 1389 (1938)
(15) Egan and Kemp, *J. Am. Chem. Soc.* **59**, 1264 (1937).
(16) Egan and Kemp, *J. Am. Chem. Soc.* **60**, 2097 (1938).

to ideal gas according to (532, 6). In the sixth column are given the values of $o\upsilon_0^K$ that have to be assumed to give agreement; when these values are assumed for $o\upsilon_0^K$ and $R \log o\upsilon_0^K$ is subtracted from the spectroscopic entropies given in the fifth column, we obtain the values given in the seventh column. It will be observed that in most, but not all, cases this value of $o\upsilon_0^K$ is unity. We need discuss only the exceptions. All the molecules are chemically saturated so that $\upsilon_0^K = \upsilon_0^G = 1$. Any deviation of $o\upsilon_0^K$ from unity must therefore be due to $o \neq 1$.

The value 2 for $o$ for $N_2O$ may be explained by supposing that the linear NNO molecule, owing to its high degree of symmetry, can, like the CO molecule, be reversed end for end without appreciably altering the energy of the crystal. The equilibrium distribution of directions will remain random down to temperatures for which $kT$ is comparable with the energy difference in the two orientations. If by this temperature the chances of reversal have become negligible, the crystal will remain for all lower temperatures with random orientations of the molecules ($o = 2$). It is interesting to observe that the SCO molecule is not sufficiently symmetrical to behave in this way. For the molecule $CH_3D$ the value 4 for $o$ takes account of the four effectively equivalent orientations of the molecule due to the D atom being isotopic with the three H atoms. We notice that the product $\sigma o$ is $3 \times 4 = 12$, equal to the value for $CH_4$ and for $CD_4$. Thus the observed behaviour of $CH_3D$ provides experimental confirmation of the rule, given in § 521, that isotopic molecules have equal values of $\sigma o$, even when the separate values of $\sigma$ and $o$ differ. We may note that for $CH_2D_2$ we should have $\sigma = 2$ and $o = 6$, so that we again recover $\sigma o = 12$.

The discrepancy between the calorimetric and spectroscopic entropies of $H_2O$ and $D_2O$ has been interpreted by Pauling* as due to an indefiniteness in the position of the hydrogen atoms, or more strictly the hydrogen nuclei, in the crystal. Pauling makes the following assumptions:

(1) In ice each oxygen atom has two hydrogens attached to it at distances about 0·95 Å. forming a molecule, the HOH angle being about 105° as in the gas molecule.

(2) Each HOH molecule is oriented so that its two H atoms are directed approximately towards two of the four O atoms which surround it tetrahedrally.

(3) The orientations of adjacent HOH molecules are such that only one H atom lies approximately along each O-O axis.

(4) Under ordinary conditions the interaction of non-adjacent molecules is not such as to stabilize appreciably any one of the many configurations satisfying the preceding conditions relative to the others.

* Pauling, *J. Am. Chem. Soc.* 57, 2680 (1935).

Pauling then calculated $o$ by two alternative methods, which lead to the same conclusion. We quote both.

A given molecule can orient itself in six ways satisfying condition 2, but the chance that the adjacent molecules will permit a given orientation is $(\frac{1}{2})^2$, since each adjacent molecule has two tetrahedral directions occupied and two unoccupied by H atoms; thus the chance of a given direction being available for the original molecule is $\frac{1}{2}$. We thus obtain $o = 6(\frac{1}{2})^2 = \frac{3}{2}$.

The same result is given by the following equivalent argument. If there are $N$ molecules, and if we ignore condition 1, there are $2^{2N}$ configurations satisfying conditions 2 and 3, each of the $2N$ H-nuclei having the choice of two positions one near one O atom and the other near the other. Some of these are ruled out by condition 1. Let us now consider a given O atom and four surrounding H atoms. There are $2^4 = 16$ arrangements of the 4H atoms, but of these only $(4.3)/2 = 6$ satisfy condition 1. We thus have

$$o^N = 2^{2N}(6/16)^N = (\tfrac{3}{2})^N \quad \text{or} \quad o = \tfrac{3}{2}.$$

This calculated value of $o$ is in excellent agreement with the experimental values for both $H_2O$ and $D_2O$. It is of interest to note that $H_2S$ shows no analogous effect.

There are also experimental data* for $BF_3$, $CF_4$ and $SF_6$, but the heats of evaporation have not been measured directly and so have to be computed from the dependence of the vapour pressures on the temperature. This procedure introduces an experimental uncertainty greater than that of the data in Table 6, probably about 0·4 cal./deg. mole. Within this degree of accuracy there is equality between the calorimetric entropy and the spectroscopic entropy.

**§ 534. Homogeneous gaseous equilibria.** As mentioned in § 526, the ideal method of comparison between theory and experiment is the study of homogeneous gaseous equilibria. As the crystal phase is not involved, the integration constant $\Delta \Sigma j$ can be calculated without any knowledge of $o$ or $v_0^K$. This is particularly simple for reactions involving only monatomic and diatomic molecules, when the only data required are the mass, the moment of inertia, the symmetry number, and the normal electronic state (occasionally as for NO the first excited electronic state is also involved). Unfortunately there are only a few reactions for which complete experimental data are available, and the accuracy is often not high. The most suitable data for comparison are given in Table 7. The agreement between theory and experiment is thoroughly satisfactory.

The comparison between theory and experiment can also be made through

* Eucken and Schröder, *Zeit. Physikal. Chem.* B, **41**, 307 (1938).

TABLE 7

*Comparison of observed and calculated values of* $\Delta(\Sigma j')$

| Reaction | Values of $j'$ calculated | Value of $\Delta(\Sigma j')$ calc. | Value of $\Delta(\Sigma j')$ obs. | References |
|---|---|---|---|---|
| (1) $2HCl \rightleftarrows H_2 + Cl_2$ | $j'_{H_2} = -3{\cdot}37$, $j'_{Cl_2} = 1{\cdot}35$, $j'_{HCl} = -0{\cdot}42$ | $-1{\cdot}16$ | $-1{\cdot}12 \pm 0{\cdot}2$ | (1) |
| (2) $2HBr \rightleftarrows H_2 + Br_2$ | $j'_{H_2} = -3{\cdot}37$, $j'_{Br_2} = 2{\cdot}35$, $j'_{HBr} = 0{\cdot}19$ | $-1{\cdot}40$ | $-1{\cdot}25 \pm 0{\cdot}45$ | (1) |
| (3) $2HI \rightleftarrows H_2 + I_2$ | $j'_{H_2} = -3{\cdot}37$, $j'_{I_2} = 2{\cdot}99$, $j'_{HI} = 0{\cdot}62$ | $-1{\cdot}62$ | $-1{\cdot}50 \pm 0{\cdot}12$ | (1) |
| *(4) $N_2 + O_2 \rightleftarrows 2NO$ | $j'_{NO} = 0{\cdot}84$, $j'_{N_2} = -0{\cdot}17_5$, $j'_{O_2} = 0{\cdot}53$ | $1{\cdot}30_5$ | $0{\cdot}95 \pm 0{\cdot}3$ | (1) |
| (5) $Cl_2 \rightleftarrows 2Cl$ | $j'_{Cl} = 1{\cdot}44$, $j'_{Cl_2} = 1{\cdot}35$ | $1{\cdot}53$ | $1{\cdot}40 \pm 0{\cdot}15$ | (1) |
| (6) $Br_2 \rightleftarrows 2Br$ | $j'_{Br} = 1{\cdot}87$, $j'_{Br_2} = 2{\cdot}35$ | $1{\cdot}39$ | $1{\cdot}41 \pm 0{\cdot}05$ | (1) |
| (7) $I_2 \rightleftarrows 2I$ | $j'_{I} = 2{\cdot}17$, $j'_{I_2} = 2{\cdot}99$ | $1{\cdot}35$ | $1{\cdot}35$ | (2) |
| (8) $2HD \rightleftarrows H_2 + D_2$ | $j'_{HD} = -2{\cdot}68$, $j'_{H_2} = -3{\cdot}37$, $j'_{D_2} = -2{\cdot}61$ | $-0{\cdot}62$ | $-0{\cdot}63 \pm 0{\cdot}05$ | (3) |

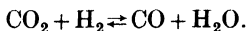
* The experimental data for this equilibrium are at high temperatures such that $T \gg 178^\circ$ K., and so the two energy levels of the doublet behave effectively as a single level with a weight $v_0^g = 2+2 = 4$. The value of $j'_{NO}$ is calculated using $v_0^g = 4$.

*References to Table 7*

(1) Eucken, *Physikal. Zeit.* **30**, 818 (1929).
(2) Gibson and Heitler, *Zeit. Phys.* **49**, 465 (1928).
(3) Rittenberg, Bleakney and Urey, *J. Chem. Phys.* **2**, 48 (1934).

the entropy changes of the reaction, as these can be determined spectroscopically and calorimetrically. Full details of this method have been described and applied by Giauque and Overstreet* to reactions 1 and 5, and by Giauque and Clayton† to reaction 4.

The same method of comparison can be applied to reactions involving polyatomic molecules. It can be illustrated by the important example of the water-gas reaction

$$CO_2 + H_2 \rightleftarrows CO + H_2O.$$

The values for the entropies of the gases at 298·1° K. and at one atmosphere, calculated from the spectroscopic data, are according to Giauque as follows:‡

$CO_2$ : 51·07, $H_2$ : 31·23, $CO$ : 47·32, $H_2O$ : 45·10 cal./deg. mole.

Thus for the reaction proceeding from left to right at 298·1° K., each chemical species being a gas at one atmosphere, the calculated increase of entropy is $\Delta S = 10{\cdot}12$ cal./deg. mole. The experimental data for the equilibrium constant at various temperatures and for the heat of reaction have been critically examined, and correlated with the heat capacities of the gases calculated from spectroscopic values by Bryant.§ The value obtained by Bryant from the experimental data for the same entropy change $\Delta S$ is 10·01 cal./deg. mole, in excellent agreement with the spectroscopic value.

The available experimental data are, however, hardly ever of sufficient accuracy to warrant such a refined method of comparison. When data for gaseous chemical equilibria become available of accuracy comparable to the vapour pressure and heat capacity data, Giauque's method of comparison can be used with advantage. At present the calculated spectroscopic data are certainly more reliable than the best experimental data for equilibrium constants.

**§ 535. Entropies of liquids, glasses and solutions.** We have seen that for isothermal processes involving only crystals of single chemical substances (a mixture of isotopes of constant composition counting as a single chemical substance) the entropy increase $\Delta S$ in the limit $T \to 0$ is given by

$$\operatorname*{Lt}_{T\to 0} \Delta S = k\Delta \log ov_0^K, \tag{535, 1}$$

and in a large majority of cases $ov_0^K$ is unity, so that $\operatorname*{Lt}_{T\to 0} \Delta S = 0$. In §§ 536–539

* Giauque and Overstreet, *J. Am. Chem. Soc.* **54**, 1731 (1932).

† Giauque and Clayton, *J. Am. Chem. Soc.* **55**, 4875 (1933).

‡ References given in Tables 5 and 6.

§ Bryant, *Ind. Eng. Chem.* **23**, 1019 (1931); *J. Soc. Chem. Ind.* **51**, 222 (1932); *Ind. Eng. Chem.* **25**, 820 (1933). The computations in the first two references have been revised in accordance with those in the last reference. The final values so obtained were communicated to us privately. They do not differ seriously from those published in the earlier articles.

we shall discuss in greater detail the conditions under which $ov_0^K$ has not the value unity. Before proceeding to this discussion for crystals of single chemical substances, we shall briefly summarize the situation for other condensed phases, that is to say liquids, glasses, and solutions.

We shall again emphasize that by $\underset{T\to 0}{\mathrm{Lt}}\, \Delta S$ we mean the value obtained for $\Delta S$ by a smooth extrapolation from the lowest convenient temperature at which measurements have been made.

The only liquid which can remain stable down to $T = 0$ is helium. For helium at the lowest temperatures reached the liquid phase is stable at low pressures, and the solid is stable at high pressures. At each temperature there is a pressure $P$ at which the two phases are in equilibrium. It has been found* that as $T \to 0$ this equilibrium pressure $P$ attains a value independent of $T$, that is to say

$$\underset{T\to 0}{\mathrm{Lt}} \frac{dP}{dT} = 0. \qquad (535,2)$$

But we have the thermodynamic relation

$$\frac{dP}{dT} = \frac{\Delta S}{\Delta V}, \qquad (535,3)$$

where $\Delta S$ and $\Delta V$ are the entropy increase and the volume increase on melting, respectively. But as $T \to 0$ the volume change $\Delta V$ was found to remain finite. Hence from (2) and (3) we deduce

$$\underset{T\to 0}{\mathrm{Lt}}\, \Delta S = 0. \qquad (535,4)$$

Thus the entropy difference between the liquid and solid forms of helium tends to zero as $T \to 0$.

All liquids other than helium become metastable at the lowest temperatures. They are usually called supercooled liquids at temperatures slightly below the melting-point, and glasses at temperatures considerably below the melting-point; the distinction is useful† but not sharp, and we shall ignore it. It was pointed out by Pauling and Tolman‡ that at a given temperature the number of distinguishable configurational states for a glass will always be greater than for a crystal, and so for the isothermal process

$$\text{crystal} \to \text{glass}$$

we must expect

$$\underset{T\to 0}{\mathrm{Lt}}\, \Delta S > 0. \qquad (535,5)$$

This can be verified experimentally by measuring on the one hand $\Delta S$ at some high temperature $T$, and on the other the heat capacities of both glass

* Keesom, *Comm. Phys. Lab. Leiden*, no. 184*b* (1926); Suppl. no. 61*b* (1927).

† Simon, *Erg. d. Exakt. Naturwiss.* **9**, 244 (1930).

‡ Pauling and Tolman, *J. Am. Chem. Soc.* **47**, 2148 (1925).

and crystal from the high temperature $T$ down to a low temperature $T^0$, from which one can extrapolate smoothly to $T = 0$. The most thoroughly investigated case is glycerol,* for which $\underset{T\to 0}{\text{Lt}}\, \Delta S$ was found to be 4·6 cal./mole deg. The corresponding value for alcohol† is 2·6 cal./mole deg. Other less completely investigated substances similarly show positive values for the limiting values of the entropy increase for the change crystal → glass.

With regard to mixtures we showed in § 520 that the entropy of a perfect mixed crystal containing $Nx$ molecules of type $A$ and $N(1-x)$ molecules of type $B$ exceeds the entropy of the component pure crystals of $A$ and $B$ at the same temperature by the amount

$$\Delta S = -Nk\{x \log x + (1-x)\log(1-x)\} > 0. \qquad (535, 6)$$

We shall see in § 815 that the same formula is applicable to liquid mixtures of a restricted class known as perfect solutions. It will, to the same restricted extent, be applicable to "perfect" glasses. Actually one cannot expect either a mixed crystal or a mixed glass to remain perfect down to the lowest temperatures, but, as long as the mixture remains homogeneous, deviations from (6) are probably not serious (see §§ 818, 819). In so far as formula (6) is valid the entropy of mixing $\Delta S$ is thus independent of temperature, and in particular retains its value as $T \to 0$. This has actually been verified‡ within the experimental accuracy of $\pm 0{\cdot}1$ cal./mole deg. for mixed crystals of AgBr and AgCl. Experimental data are also available for the process

$$\text{glycerol (liq.)} + \text{ice (cryst.)} \to \text{mixture (glass)},$$

the value of $\Delta S$ found§ by smooth extrapolation from 9° K. to 0° K. agreeing with the value given by (6) within the experimental accuracy of $\pm 0{\cdot}4$ cal./mole deg. Actually one would expect formula (6) to apply rather to the process

$$\text{glycerol (liq.)} + \text{water (liq.)} \to \text{mixture (glass)}.$$

**§ 536. The third law of thermodynamics. (i) The experimental values of** *o*. We are now due to undertake a discussion of the third law of thermodynamics and Nernst's heat theorem. The law and the theorem have been in the past subject to much controversy, but one may perhaps claim that substantial agreement has recently been achieved. We shall therefore follow our usual practice in this book and give a purely didactic exposition of the law and the theorem, in what we believe to be the most satisfactory form. In view, however, of recent controversies we shall start

* Simon and Lange, *Zeit. Phys.* **38**, 227 (1926). Cf. Gibson and Giauque, *J. Am. Chem. Soc.* **45**, 93 (1923).

† Kelley, *J. Am. Chem. Soc.* **51**, 779 (1929).

‡ Eastman and Milner, *J. Chem. Phys.* **1**, 444 (1933).

§ Simon, *Handb. d. Physik*, **10**, 393.

with a discussion of the meaning of the experimental values of $ov_0^K$, followed by a short historical introduction, before we give the statement of the third law and develop its consequences.

In discussing Nernst's heat theorem we are concerned with the behaviour of the entropy change in an isothermal reaction when $T \to 0$. The discussions of the earlier part of this chapter have shown us that.

*For any isothermal reactions between pure crystals*

$$\underset{T\to 0}{\mathrm{Lt}}\ \Delta S = k\Delta\Sigma \log ov_0^K. \tag{536, 1}$$

They have shown us further how in practice this limit is evaluated, and have made a number of determinations of $ov_0^K$ for various crystals. We shall consider these determinations in greater detail here.

We have seen that usually $ov_0^K = 1$. The occasional values of $ov_0^K > 1$ can arise in two distinct ways which we consider in turn.

(*a*) *Extrapolation from too high a value of* $T^0$. We emphasize again that we cannot make measurements at the absolute zero, and the only physical meaning for a quantity such as $\Delta S$ at the absolute zero is the limit of this quantity as $T \to 0$. The evaluation of this limit will always involve an extrapolation to $T = 0$ from the lowest convenient temperature $T^0$ for which measurements of heat capacities have been made. In our theoretical formulae various sets of states are treated as degenerate, but none of these sets need be strictly degenerate; so long as their energy differences $\Delta\epsilon$ are small compared with $kT$, it is correct to ignore these differences and treat the set simply as a degenerate state with the corresponding extra weight factor. If the observations stop at a temperature $T^0$ sufficiently high, no effect of the ignored separations will be seen in the heat capacities, and one must include the extra weight factors in the partition function. If, however, observations are pushed lower ($kT^0 \simeq \Delta\epsilon$), we reach temperatures at which, for equilibrium to be maintained, the upper states of the set must be gradually emptied. Finally we may reach still lower temperatures ($kT^0 \ll \Delta\epsilon$) where the upper states can be ignored, and the effective states are no longer degenerate or at least not so highly degenerate. During this change the heat capacity will show temporarily exceptionally large values, and the extra weight factors removed from $k \log ov_0^K$ are replaced by an equal contribution from the double integral

$$\int_{T^0}^{T} \frac{dT_1}{T_1^2} \int_{T^0}^{T_1} C^K(T_2)\, dT_2. \tag{536, 2}$$

It is easily verified that, if $T$ lies in a range in which $\varpi_0 + \varpi_1$ states per molecule have a negligible and all others a large energy compared with $kT$, while $T^0$ lies in a range in which only $\varpi_0$ states have a negligible and all others

a large energy compared with $kT^0$, the integral (2) contributes precisely $k\log(\varpi_0+\varpi_1)-k\log\varpi_0$. This is just the difference between $[k\log ov_0^K]_T$ and $[k\log ov_0^K]_{T^0}$, where the subscripts $T$ and $T^0$ indicate the temperatures from which a smooth extrapolation of the heat capacity is made.

We have already seen in § 531 that ortho-hydrogen, and to a less extent the ordinary metastable mixture of ortho- and para-hydrogen, shows a rise in the heat capacity when the temperature is reduced below 12° K. For $H_2$ undoubtedly $v_0^K = v_0^G = 1$, and so we need consider only the orientational weight factor $o$. The values $o = 3$ for ortho-hydrogen and $o = 3^{\frac{3}{4}}$ for the ordinary metastable mixture are evidently due to too high a choice of $T^0$. If the heat capacity measurements could be continued to still lower temperatures, and the double integral (2) were evaluated with the limits 0·3° K. and 12° K., its value would be $k\log 3$ for ortho-hydrogen or $\frac{3}{4}k\log 3$ for ordinary hydrogen. One would then be able to choose $T^0 \simeq 0{\cdot}3°$ K. and would find $o = 1$. Similarly the weight factors $o = 3$ for para-deuterium and $o = 3^{\frac{1}{3}}$ for the ordinary mixture of ortho- and para-deuterium would be reduced to unity by using a sufficiently low $T^0$. Thus for reactions involving $H_2$ and $D_2$ extrapolated to zero from $T^0 \simeq 0{\cdot}3°$ K. no contribution would be expected towards a non-zero value of $o$ by the $H_2$ or $D_2$ involved.

(*b*) *Frozen-in varieties of orientation.* There are a number of other molecules CO, NO, $N_2O$, $H_2O$ and $D_2O$ whose crystals have non-unit values of $o$ and so of $ov_0^K$. These extra weight factors we have attributed to extra orientations of one type or another—for CO and NNO to the possibility of turning an almost symmetrical linear molecule end for end; for NO to the possibility of two distinct orientations for the molecule $N_2O_2$; for $H_2O$ and $D_2O$ to the possible different arrangements of the H or D (§ 533). The energy differences of these orientations are small, and for any example it may be that the various orientations form a still effectively degenerate but unfrozen state at $T^0$, so that the extra weight factor would be removed by choice of a lower $T^0$, an example of case (*a*). This however is unlikely. It is much more likely that we have a case of metastable equilibrium with the random orientations frozen in. In general we should perhaps expect such metastable equilibria, whenever we have a crystal built of molecules with their two ends physically distinguishable but extremely similar in size and force field. The same expectation may clearly be extended to more complicated molecules, where the same or similar conditions hold. For we may then expect the molecule to have two or more equilibrium orientations in the crystal, only one of which is completely stable, the remainder being metastable, leading to a value of $o > 1$. The metastable orientations lie above the stable orientation by an energy difference $\Delta\epsilon$, which is much smaller than $kT_k$, where $T_k$ is the minimum temperature required for reorientation at an appreciable

speed. In other words when we reach temperatures so low that it matters to the molecule which way it points, it is already practically impossible for it to turn round. The situation is exactly the same for orientations here as it is for spatial arrangements and rearrangements in a glass or in a chilled metallic alloy and we might describe such phases as "orientationally amorphous". The molecules will remain frozen at all lower temperatures, being distributed perfectly at random between their two or more orientations. The frozen crystal with $o$ orientations occupied at random will have an entropy $k \log o$ per molecule greater than an ideal crystal with regular orientations, and this is the entropy which one would naturally regard as the true limiting value of its entropy at the absolute zero. It is interesting to note that, for an almost symmetrical molecule of the type discussed here, we obtain the correct value of its vapour pressure constant by treating it as truly symmetrical; for then we replace the true values $o = 2$, $\sigma = 1$ by the fictitious values $o = 1$, $\sigma = 2$, and the product $o\sigma$ is unaltered.

In concluding this section we may note one further possibility, at least for ideal experiments, of which we have not taken account hitherto. All our formulae are based on the assumption that for a symmetrical molecule $X_2$ there is no ortho-para conversion in any phase at low temperatures, but that the ortho-para ratio remains fixed at the value characteristic of high temperature equilibrium. We have seen moreover that ortho-para separations as such make no contribution to the limiting values of $\Delta S$ as $T \to 0$, except by accident when extrapolations are made from too large a value of $T^0$. Now the crystal state constructed from the ortho-para mixture is a metastable one, and it might be possible to replace it by the true stable state at all temperatures by using suitable experimental methods. For example, hydrogen can be reduced with reasonable rapidity to its true equilibrium state by using a suitable catalyst; the reduction to practically pure parahydrogen is completed in the liquid phase, and, if this is done, the resulting solid phase will differ insignificantly from the true equilibrium state for all temperatures in question. Ideally it must be possible to treat all other molecules $X_2$ in the same way, though in fact there would be great practical difficulties, since it is only for hydrogen and deuterium that the reduction to the pure state would be practically completed before the freezing-point is reached.

Suppose now we try to improve our current practice by using hydrogen catalysed into the true equilibrium state instead of the ortho-para mixture, and applying the thermal data so obtained to evaluate $\mathrm{Lt}_{T \to 0} \Delta S$ for reactions between solids involving hydrogen. We shall still find that it is not true in general that $\Delta S \to 0$, even if we imagine that the solid phases of all the molecules concerned can be and are catalysed to true equilibrium. For the

catalysis to para-hydrogen (for example) removes not merely the redundant $o$-factor $3^{\frac{3}{4}}$ per $H_2$ molecule, replacing it by an extra contribution from the integral (2), but also in the same way the nuclear spin weights and the entropy of mixing, since the equilibrium state is pure para-hydrogen whose ground state has weight unity including nuclear spins. The nuclear spin weight and the entropy of mixing together contribute a spin weight 2 per H atom. This spin weight 2 per H atom will survive as usual in the other solid phases, and the nuclear spin term $k\Sigma \log \rho$ will no longer cancel from $\Delta S$ and other thermodynamic formulae. Thus while experiments on the normal ortho-para mixture $H_2$ yield a contribution $\pm \frac{3}{4}k \log 3$ to $\Delta S$, those on catalysed $H_2$ would yield $\mp k \log 4$ per molecule, the term actually arising from the surviving spins in the unsymmetrical molecules on the other side of the reaction equation.

The removal of the spin weights, which is thus actually feasible at present for $H_2$ and $D_2$ but probably not for any other substance, is due to the coupling of the nuclear spins to the molecular rotations demanded by the symmetry requirements. This means that energy differences which are very large from the points of view of nuclear spins are effectively dependent on the spins, and can therefore be eliminated at accessible temperatures together with the nuclear spin degeneracies associated with them. In heteronuclear molecules on the other hand, where the spins are not coupled by the symmetries to such large energy differences, no such elimination is possible at these temperatures.

**§ 537. The third law of thermodynamics. (ii) Historical sketch.** After this introductory survey of the statistical interpretation of the experimental facts in the form of observed values of $ov_0^K$, we pass to a brief historical sketch of the third law of thermodynamics and Nernst's heat theorem, particularly of the various enunciations of the theorem.*

One of the earliest enunciations of Nernst's heat theorem took the form: *In any isothermal process between condensed phases (including glasses, supercooled liquids and solutions)*

$$\operatorname*{Lt}_{T\to 0} \Delta S = 0. \qquad (537, 1)$$

Provided we assign to $\operatorname*{Lt}_{T\to 0}$ the usual meaning corresponding to a smooth extrapolation, we saw in § 535 that (1) is not true either for glasses or for solutions.

* See Nernst, *Die theoretischen und experimentellen Grundlagen des neuen Warmesatzes*, Ed 2 (1924) The reader should also refer to Simon, "Funfundzwanzig Jahre Nernstschen Wärmesatzes", *Erg. d. Exakt. Naturwiss.* **9**, 222 (1930), a valuable article recording much work which has played an essential part in the elimination of the earlier errors

It was therefore necessary to revise the enunciation, and restricted enunciations of the theorem were later proposed in the forms:

(*a*) *For any isothermal process involving only pure crystals*

$$\operatorname*{Lt}_{T\to 0} \Delta S = 0. \tag{537, 2}$$

(*b*) *If the entropy of each element in the crystalline state stable at $T = 0$ be taken as zero, every substance has then a finite positive entropy, but at $T = 0$ the entropy may become zero, and does become zero for all perfect crystalline substances including compounds.*

Formulation (*b*) is equivalent to one first given by Lewis and Gibson.* It will be observed that they are careful so to formulate the theorem that the idea of absolute entropy is not introduced.

These enunciations avoid the difficulty created by phases such as glasses, ordinarily recognized as amorphous, but the empirical foundations even of these enunciations soon became none too secure as the facts became better known. Further progress in the understanding of the theorem has been greatly helped by a better appreciation of its statistical interpretation through studies of the formula (535, 1) and especially of the conditions under which we may expect $o = 1$ for all substances concerned in any reaction. But however wide or narrow these conditions turn out to be, it is already clear that the theorem $\Delta S \to 0$ is not universally valid according to its normal interpretation. It was therefore natural to search for a suitable principle of universal validity which might rank as a third law of thermodynamics and from which Nernst's heat theorem when true would follow.

Such a principle, fulfilling all requirements, is available—*The principle of the unattainability of the absolute zero*, first enunciated by Nernst.† We shall adopt this principle as the third law, and proceed in the following sections to state it in a precise form and to derive from it a correct version of Nernst's heat theorem, which we can then compare with our statistical analysis of the facts.

**§ 538. The third law of thermodynamics. (iii) Its thermodynamic formulation and consequences.** The principle of the unattainability of the absolute zero on the available evidence is of completely general validity. This principle, which we call the *third law of thermodynamics*, may be more precisely enunciated as follows:

*It is impossible by any procedure, no matter how idealized, to reduce any assembly to the absolute zero in a finite number of operations.*

The type of evidence that suggests this principle most strongly is that

* Lewis and Gibson, *J. Am. Chem. Soc.* **42**, 1529 (1920). See also Lewis and Randall, *Thermodynamics*, p. 448 (McGraw-Hill, 1923). † Nernst, *Berlin. Sitzungsber.* p. 134 (1912).

derived from experiments on the adiabatic demagnetization of paramagnetic salts, the discussion of which will be found in Chapter XIV. Accepting the principle, we proceed to examine its consequences.*

Let us consider any process (e.g. change of volume, change of external field, chemical reaction) denoted formally by

$$\alpha \to \beta; \tag{538, 1}$$

we shall use the subscripts $\alpha$ and $\beta$ to denote properties of the assembly in the states $\alpha$ and $\beta$ respectively. Then the entropies of the assembly in these two states depend on the temperature according to the formulae

$$S_\alpha = S_\alpha^0 + \int_0^T \frac{C_\alpha}{T} dT, \tag{538, 2}$$

$$S_\beta = S_\beta^0 + \int_0^T \frac{C_\beta}{T} dT, \tag{538, 3}$$

where $S_\alpha^0$, $S_\beta^0$ are the limiting values of $S_\alpha$, $S_\beta$ for $T \to 0$. We know from quantum theory that both the integrals converge. Suppose now that we start with the assembly in the state $\alpha$ at the temperature $T'$, and that we can make the process $\alpha \to \beta$ take place adiabatically. Let the final temperature after the assembly has reached the state $\beta$ be $T''$. We are now going to consider the possibility or impossibility of $T''$ being zero. From the second law of thermodynamics we know that, for a process defined by its initial and final states, the change of entropy is zero if the process takes place quasi-statistically but positive otherwise. It is therefore clear that the chances of attaining as low a final $T$ as possible are most favourable when the process takes place quasi-statically. We need therefore consider only such a quasi-static path. For the quasi-static adiabatic process being considered we have then by (2) and (3)

$$S_\alpha^0 + \int_0^{T'} \frac{C_\alpha}{T} dT = S_\beta^0 + \int_0^{T''} \frac{C_\beta}{T} dT. \tag{538, 4}$$

If $T''$ is to be zero, we must then have

$$S_\beta^0 - S_\alpha^0 = \int_0^{T'} \frac{C_\alpha}{T} dT. \tag{538, 5}$$

Now if $S_\beta^0 - S_\alpha^0 > 0$, it will always be possible to choose an initial $T'$ satisfying (5), and by making the process $\alpha \to \beta$ take place from this initial $T'$ it will be possible to reach $T'' = 0$. From the premise of the unattainability of

* The following discussion is essentially equivalent to that given by Simon [*Science Museum Handbook*, Book 3, p. 61 (1937)]. All other discussions, that we know of, make unnecessary restrictions concerning the temperature dependence of the heat capacities. It should be noticed that the only assumption here made is that as $T \to 0$ the heat capacities all tend to zero sufficiently fast for the entropies to remain finite.

$T = 0$ we can therefore conclude that

$$S^0_\beta \leqslant S^0_\alpha. \tag{538, 6}$$

Similarly we can show that, if we can make the reverse process $\beta \to \alpha$ take place quasi-statically and adiabatically, then we can reach $T = 0$ from an initial temperature $T'$ satisfying

$$S^0_\alpha - S^0_\beta = \int_0^{T'} \frac{C_\beta}{T} dT. \tag{538, 7}$$

Further, if $S^0_\alpha - S^0_\beta > 0$, we can always choose an initial $T'$ satisfying (7). From the unattainability of $T = 0$ we can therefore conclude that

$$S^0_\alpha \leqslant S^0_\beta. \tag{538, 8}$$

From (6) and (8) we deduce

$$S^0_\alpha = S^0_\beta. \tag{538, 9}$$

This is precisely Nernst's heat theorem.

We can also show conversely that, given (9), neither the process $\alpha \to \beta$ nor the reverse process $\beta \to \alpha$ can be used to reach $T = 0$. For, assuming (9) to be true, we now have for the adiabatic process $\alpha \to \beta$ the initial temperature $T'$ and the final temperature $T''$ related by

$$\int_0^{T'} \frac{C_\alpha}{T} dT = \int_0^{T''} \frac{C_\beta}{T} dT. \tag{538, 10}$$

To reach $T'' = 0$ we should require

$$\int_0^{T'} \frac{C_\alpha}{T} dT = 0. \tag{538, 11}$$

But since $C_\alpha > 0$ always for any finite $T$, it is impossible to satisfy (11). Hence the process $\alpha \to \beta$ cannot be used to reach $T = 0$. The proof for the reverse process $\beta \to \alpha$ is exactly similar.

From the derivation of Nernst's heat theorem in the form (9) we see that its deduction from the third law of thermodynamics (the unattainability of $T = 0$) involves the assumption that the states $\alpha$ and $\beta$ can be connected by a reversible path.

If all the phases concerned are phases in complete internal equilibrium, the reactions concerned must presumably be regarded as ideally reversible. If any phase is naturally in metastable internal equilibrium, a reaction or process affecting it may or may not disturb the frozen metastable equilibrium. If it does not disturb this equilibrium, then the reaction or process must still be regarded as reversible, but otherwise it will be irreversible. We may therefore enunciate *Nernst's heat theorem* in the following accurate form:

*For any isothermal process involving only phases in internal equilibrium or, alternatively, if any phase is in frozen metastable equilibrium, provided*

*the process does not disturb this frozen equilibrium,*

$$\operatorname*{Lt}_{T\to 0} \Delta S = 0. \tag{538, 12}$$

This includes all physical changes which depend on the variation of some continuous external parameter such as pressure or magnetic field strength. It also covers all chemical reactions between phases in internal equilibrium, but does not include chemical reactions involving phases in metastable equilibrium.

Any conceivable isothermal process involving a phase in frozen metastable equilibrium, which does disturb the metastability, can obviously proceed only in the direction which decreases this metastability. It follows at once from the third law that for such a reaction proceeding in the only possible direction

$$\operatorname*{Lt}_{T\to 0} \Delta S < 0, \tag{538, 13}$$

and such a process is even less efficient* for reaching $T = 0$ than one for which $\operatorname*{Lt}_{T\to 0} \Delta S = 0$.

**§ 539. The third law of thermodynamics. (iv) Statistical interpretation.** We are now in a position to give a proper statistical interpretation of Nernst's heat theorem. We have seen in the earlier sections of this chapter, whose results are collected and discussed in § 536 that, for all reactions between crystals,

$$\operatorname*{Lt}_{T\to 0} \Delta S = k\Delta \Sigma \log ov_0^K, \tag{539, 1}$$

in calculating which all contributions of nuclear spins, isotopic mixtures and ortho-para separations can be ignored. Further, provided that extrapolations are made to zero from a suitably chosen $T^0$, which is of the order commonly used in practice (except that, for $H_2$ and for $D_2$, $T^0$ should be about 0·3° K.), we have also found that $ov_0^K$ is different from unity only for orientationally amorphous phases in frozen metastable equilibrium. For these phases $o > 1$ and so $ov_0^K > 1$. Hence for any process which thaws or removes the metastability

$$\operatorname*{Lt}_{T\to 0} \Delta S < 0. \tag{539, 2}$$

For any process on the other hand which does not concern systems for which $ov_0^K > 1$, or in which values of $ov_0^K$ if greater than unity occur but are not affected,

$$\operatorname*{Lt}_{T\to 0} \Delta S = 0. \tag{539, 3}$$

These statistical conclusions are therefore in full agreement with the third law and our deductions from it.

It has been argued† that irregular solid phases must be excluded from the

* See Simon, *Zeit. Phys.* **41**, 806 (1927).

† Simon, *Zeit. Anorg. Chem.* **203**, 226 (1931).

field of the theorems *a priori*, because, since they are phases in metastable equilibrium and not in true internal equilibrium, the theorems of thermodynamics, including Nernst's heat theorem, which state equalities, cannot be applied to them. This point of view, however, proves too drastic and cannot be reasonably maintained.* In its extreme form this view implies that a phase in frozen equilibrium has no definite value of the entropy. In the first place we observe that there is no need to hold this view in order to be able to give a perfectly general and acceptable form of the third law of thermodynamics and Nernst's heat theorem, such as we have given above. Again an entropy difference between a metastable solid phase and the liquid phase can always be established and measured, because by carrying out the melting process at the proper speed it can be made to go reversibly, or practically reversibly. In the particular case of NNO it has been shown† that the thermal properties of the crystal at the lowest temperatures are entirely independent of the rate of cooling to these temperatures. It follows that the changes occurring during heating and cooling are reversible, although the crystal, being orientationally amorphous, is unquestionably metastable at the lowest temperatures. Thus the metastable solid phase must be held to have a definite entropy, just as much as any other phase in which the substance can exist.

It is argued again that a glass cannot have a definite vapour pressure. This may well be true. For if the process of evaporation and recondensation removes the metastability, the vapour pressure would progressively change over to the vapour pressure characteristic of the regular crystalline solid. But even if it is true that a particular glass has no vapour pressure, this does not mean that the glass has no definite entropy, but merely, as is obvious, that the process of evaporation is irreversible. On the other hand it is conceivable that the process of evaporation from an irregular solid like a glass is in the absence of the crystalline form actually reversible, and that the recondensation on the amorphous substance leaves the solid amorphous. In this case the glass would resemble a supersaturated solution in having a definite vapour pressure in spite of its metastability.

A well-known assembly to which no one hesitates to apply the theorems of thermodynamics is a gaseous mixture of oxygen and hydrogen. This is only in metastable equilibrium, since in the true equilibrium state there should be a large conversion of the oxygen and hydrogen into water or steam. The difference of entropy (or of free energy) between such a metastable assembly and the stable assembly into which it might be changed irreversibly has a well-defined and measurable value.

* Compare Eastman and Milner, *J. Chem. Phys.* 1, 451 (1933).

† Eucken and Veith, *Zeit. Physikal. Chem.* B, 35, 463 (1937).

Careful consideration of all such cases leads to the conclusion that all thermodynamic systems are liable to be only metastable, and all applications of the equalities stated by the theorems of thermodynamics to be of only relative validity. Actually we hardly ever, if ever at all, deal with complete equilibrium in the strict sense of the word,* for even among elementary atoms probably some are unstable relative to others, but, except for the recognizably radioactive elements, the transformations are negligibly slow. The fact that there are such slow transformations occurring does not, however, matter to thermodynamics. In order to be able to use the equalities stated by its theorems we must be able to classify all processes of change into two classes, those that are very fast and those that are very slow compared with the changes that we wish to impose experimentally. The processes of the slow group we can entirely ignore. Those of the fast group will maintain complete equilibrium among the states or phases that they connect, and the imposed changes will be perfectly reversible. Processes of intermediate speed which are neither fast nor slow are, however, fatal, and inevitably make an imposed change irreversible. The situation in pure thermodynamics is in fact exactly the same as we found it in discussing the underlying principles of accessibility in statistical mechanics in § 105. There seems no good reason for supposing that processes and phenomena at very low temperatures are any different in this respect from those at ordinary temperatures, to which we are better accustomed, and there is no need to make such artificial distinctions in order to preserve a general form of Nernst's heat theorem.

**§ 540. Homogeneous equilibrium in an external field.** All the formulae of this chapter so far refer to assemblies subject to no external fields of force, except the local boundary fields. This restriction can easily be removed for the gaseous part of the assembly, for which alone it is of importance. We will suppose that classical statistics may be used, and that all the gaseous components are confined to the same volume $V$. Then in the partition function of $A$ we have to replace the factor $V$ by

$$\int_V e^{-u_A/kT}\, dV, \qquad (540,1)$$

where $u_A$ denotes the potential energy of a molecule $A$ in the particular volume element $dV$. We have therefore

$$f_A(T) = \phi_A(T)\int_V e^{-u_A/kT}\, dV, \qquad (540,2)$$

where $\phi_A(T)$ has the same value throughout the volume $V$. If $N_A$ is the

* Giauque and Johnston, *Phys. Rev.* **36**, 1592 (1930).

total number of molecules $A$, then, as we have already seen in § 304, the average number $n_A(\delta V_r)$ in the particular volume element $\delta V_r$ is given by

$$n_A(\delta V_r) = N_A \frac{e^{-u^r_A/kT}\,\delta V_r}{\int_V e^{-u_A/kT}\,dV}. \qquad (540, 3)$$

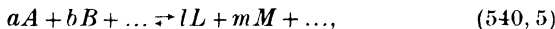
This determines the equilibrium between one volume element and another.

Let us now consider only the molecules in the volume element $\delta V_r$. The molecules $A$ in this element have the partition function $\delta f_A(T)$ given by

$$\delta f_A(T) = \phi_A(T)\, e^{-u^r_A/kT}\,\delta V_r, \qquad (540, 4)$$

and similar relations hold for each type of molecule.

From the form of (4) we can deduce that the equilibrium condition for the gaseous reaction

$$aA + bB + \ldots \rightleftarrows lL + mM + \ldots, \qquad (540, 5)$$

in the particular volume element $\delta V_r$, takes the form

$$\Pi_L\,(c^r_L)^l / \Pi_A\,(c^r_A)^a = K = K^0\, e^{-(\Sigma_L l u_L - \Sigma_A a u_A)/kT}, \qquad (540, 6)$$

where each $c^r$ denotes a concentration in the volume element $\delta V_r$, and

$$K^0 = \Pi_L\,(\phi_L)^l / \Pi_A\,(\phi_A)^a, \qquad (540, 7)$$

so that $K^0$ has the same value throughout the volume $V$. We can verify that the equilibrium distribution law (3) for each type of molecule is consistent with the space variation (6) of the equilibrium constant. In general the value of the equilibrium constant $K$ will vary from one volume element to another. But in the two most important applications it will not vary.

(1) In a gravitational or centrifugal field we have

$$\frac{u_A}{m_A} = \frac{u_B}{m_B} = \ldots = \frac{u_L}{m_L} = \frac{u_M}{m_M} = \ldots, \qquad (540, 8)$$

where $m$ denotes the mass of a molecule. Hence

$$\Sigma_L\, l u_L = \Sigma_A\, a u_A, \qquad (540, 9)$$

because of the conservation of mass.

(2) For molecules (ions) of electric charge $z_A|e|$ in an electric field we have

$$\frac{u_A}{z_A} = \frac{u_B}{z_B} = \ldots = \frac{u_L}{z_L} = \frac{u_M}{z_M} = \ldots, \qquad (540, 10)$$

and so again

$$\Sigma_L\, l u_L = \Sigma_A\, a u_A, \qquad (540, 11)$$

because of the conservation of charge.

Hence for both these cases

$$K = K^0 \qquad (540, 12)$$

and is independent of the potential.

On the other hand, for molecules with an electric (or magnetic) moment in an external electric (or magnetic) field the equilibrium constant $K$ will depend on the field strength because in a chemical change electric (or magnetic) moments are not necessarily conserved.

## CHAPTER VI

### GRAND PARTITION FUNCTIONS AND THEIR APPLICATIONS

**§ 600. Introduction.** We shall now describe a more general and powerful statistical method than any we have explicitly used hitherto. This method involves no new assumption but merely a rearrangement of the formulae used, and is the quantal analogue of Gibbs' use of the *grand canonical ensemble*, introduced by him in the last chapter of his *Introduction to Statistical Mechanics.**

As we have already mentioned in Chapter I, Gibbs' normal method of procedure is to determine the equilibrium properties of an assembly or a phase by averaging the properties of the assembly over an ensemble of examples canonically distributed in phase, keeping the numbers of systems in the assembly fixed. This means, as we can now see, merely constructing the partition function for the assembly by summing or integrating over the whole of accessible phase space for a fixed number of the systems constituting the assembly. In his last chapter§ Gibbs removes the restriction to a fixed number of systems, and derives the equilibrium properties of the assembly or phase by summing

$$e^{(N_A\mu_A+N_B\mu_B+\ldots-E)/kT} \tag{600, 1}$$

over all values of the $N_A$, $N_B$, ..., and over the whole of accessible phase space for each set of values of the $N$'s. He calls the family of the assemblies so contemplated *a grand ensemble canonically distributed in phase*. It would seem natural therefore to apply a somewhat similar name to the statistical function so constructed. We shall show in this chapter how one may conveniently proceed by summing or integrating the equivalent functions

$$\lambda_A^{N_A}\lambda_B^{N_B}\ldots\vartheta^E \tag{600, 2}$$

over all $N$'s and all accessible states or phase space. We shall call this function *a grand partition function for the assembly*, thereby perpetuating Gibbs' nomenclature.†

It may be well to pause a moment to consider the physical meaning of this type of construction, which leaves the $N$'s unspecified *a priori*, compared with the normal method of procedure which keeps them all fixed at given values. We recall that initially in Chapter II we considered an assembly

* An excellent account of the classical form of this method is given by Landau and Lifschitz, *Statistical Physics*, sect. 46 (Oxford, 1937).

§ Gibbs, *Elementary Principles in Statistical Mechanics*, Chapter XV, *Collected Works*, **2** (Longmans, 1928).

† See Fowler, *Proc. Camb. Phil. Soc.* **34**, 382 (1938).

with a specified total energy $E$, and were led by natural reasoning to the conception of the statistical temperature $\vartheta$. We obtained a relation between $\vartheta$ and $E$. Its manner of derivation there corresponded to regarding $\vartheta$ as determined by $E$, but we pointed out that it was equally allowable, and usually more convenient, to regard $E$ as determined by $\vartheta$. Physically this change of point of view corresponds to considering an assembly in a thermostat instead of an isolated assembly. The interrelationships of the $\lambda$'s and the $N$'s is exactly parallel to that of $\vartheta$ and $E$. In previous chapters we have considered the $N$'s as given, and we have regarded the $\lambda$'s as determined by the $N$'s, whereas now we wish to invert the relations and regard the $N$'s as determined by the $\lambda$'s. Physically this means that instead of considering a completely enclosed assembly or phase we consider one in intimate contact with another (very large) phase, say a gaseous phase, of given temperature and composition, which is not regarded as part of the assembly. The temperature and composition of the large subsidiary phase fix $\vartheta$ and the $\lambda$'s, and, if the phase is large enough, fix them at values unaffected by any parts taken up by the assembly proper. We then determine the equilibrium properties of the assembly proper in equilibrium with this given surrounding medium. This, as we shall see, is most expeditiously done by constructing the grand partition function.

The connection between thermodynamics and statistical mechanics with the use of grand partition functions* may be made even more simply, though somewhat more abstractly, than in the usual manner. Its development, however, requires the use of some of the less familiar thermodynamic relations, and we shall therefore recall shortly in the next section some which we shall use later.

§ 601. **Some special thermodynamic potentials.** For the sake of brevity we shall write all formulae for a single phase assembly. The more general formulae for assemblies of several phases are directly obtainable by introducing the appropriate summations; it is, however, one of the chief merits of the new approach which we are about to develop, that it is always easy and indeed natural to confine attention to a single phase assembly, whereas this is not always possible for the usual statistical method which uses given $N$'s.

We can start with formula (222, 18) which, for a single phase with only a single geometrical parameter $x$, becomes

$$dF = -S\,dT - X\,dx + \Sigma_A \mu_A dN_A. \qquad (601, 1)$$

We shall assume that the geometrical parameter $x$ is of the nature of a volume

* Cf. Pauli, *Zeit. Phys.* **41**, 88 (1927); Delbrück and Molière, *Abh. Preuss. Akad. Wiss.* no. 1 (1936).

or a surface area defining the size of the assembly. Then at any given temperature $F$ is homogeneous and of the first degree in $x$ and the $N$'s, and therefore by Euler's theorem

$$F = x\frac{\partial F}{\partial x} + \Sigma_A N_A \frac{\partial F}{\partial N_A} = -Xx + \Sigma_A N_A \mu_A. \qquad (601, 2)$$

We can now define a function $G$ in the usual manner by the equation

$$G = F + Xx, \qquad (601, 3)$$

which may be shown, by differentiation of (3) and the use of (1), to have the property that

$$dG = -SdT + xdX + \Sigma_A \mu_A dN_A. \qquad (601, 4)$$

We notice that (4) is the fundamental equation for the variables $T$, $X$, and the $N$'s, so that $G$ is a thermodynamic potential for this set of variables, which in virtue of its introduction by Gibbs will be called the Gibbs function.*

By using (3) we can write (2) in the alternative form

$$G = \Sigma_A N_A \mu_A. \qquad (601, 5)$$

By differentiating (5) and combining the result with (4) we obtain the relation

$$SdT - xdX + \Sigma_A N_A d\mu_A = 0, \qquad (601, 6)$$

usually known as the Gibbs-Duhem relation. These formulae are all classical, and will be familiar to every student of Gibbs' works.†

We now pass on to variations of these formulae which may be less familiar. We can rearrange (2) in the form

$$Xx = \Sigma_A N_A \mu_A - F; \qquad (601, 7)$$

differentiating this and using (1) we obtain

$$d(Xx) = SdT + Xdx + \Sigma_A N_A d\mu_A. \qquad (601, 8)$$

Equation (8) is the fundamental equation for the variables $T$, $x$ and the $\mu$'s. It follows that $Xx$ is a thermodynamic potential for these variables. From (8) we derive immediately

$$\partial(Xx)/\partial T = S, \qquad (601, 9)$$

$$\partial(Xx)/\partial x = X, \qquad (601, 10)$$

$$\partial(Xx)/\partial \mu_A = N_A. \qquad (601, 11)$$

* The nomenclature for the various thermodynamic potential is unfortunately confusing. We mention for clarity that $F$, which we here call the free energy (name due to Helmholtz), is also called the free energy of Helmholtz or the work function and is identical with Gibbs' $\psi$. The Gibbs function $G$ is identical with Gibbs' $\zeta$ and is also called the free energy of Gibbs or even the free energy and sometimes the thermodynamic potential. The last two names are indefensible.

† For the convenience of any reader referring to Gibbs we note that formulae (1), (4), (6) here correspond to Gibbs' formulae (88), (92) and (97); see Gibbs, *Collected Works*, 1, 87 sqq. (Longmans, 1928).

It turns out that it may be easier to construct the potential $Xx(T, x, \mu_A, \ldots)$ as a function of the specified variables for many complicated assemblies or phases, than it is to construct the free energy. This will become clear in later sections where we actually construct $Xx$ statistically.

**§ 602. Statistical formulae for $Xx$.** In order to make effective use of the thermodynamic potential $Xx$ we require statistical formulae for its evaluation. In the simple case of a gaseous assembly these are derivable at once from those already obtained for $F$ and the $\mu$'s. We have according to (224, 5) and (226, 6)

$$F = -kT\,\Sigma_A\,\Sigma_r\,\varpi_r \log(1 \pm \lambda_A e^{-\epsilon_r/kT})^{\pm 1} + kT\,\Sigma_A\,N_A \log \lambda_A, \quad (602, 1)$$

and according to (224, 9)

$$\mu_A = kT \log \lambda_A. \quad (602, 2)$$

As already mentioned in § 224, an appropriate thermodynamic name for $\lambda_A$ is the *absolute activity* of $A$. From (1), (2) and (601, 7) it follows at once that

$$Xx = kT\,\Sigma_A\,\Sigma_r\,\varpi_r \log(1 \pm \lambda_A e^{-\epsilon_r/kT})^{\pm 1}. \quad (602, 3)$$

It is noteworthy that this formula for $Xx$ is simpler than formula (1) for $F$, and still simpler than formula (224, 18) for the entropy. By using (2) we can write (3) in the alternative form

$$Xx = kT\,\Sigma_A\,\Sigma_r\,\varpi_r \log(1 \pm e^{[\mu_A - \epsilon_r]/kT})^{\pm 1}. \quad (602, 4)$$

It is convenient for brevity to rewrite (3) in the form

$$Xx = kT \log \Xi, \quad (602, 5)$$

where

$$\Xi = \Pi_A\,\Pi_r\,(1 \pm \lambda_A e^{-\epsilon_r/kT})^{\pm \varpi_r} \quad (602, 6)$$

$$= \Pi_A\,\Pi_r\,(1 \pm \lambda_A \vartheta^{\epsilon_r})^{\pm \varpi_r}.$$

We now observe that $\Xi$ was constructed in § 214 for this phase, with the precise object of having the property that the coefficient of $\lambda_A^{N_A}\lambda_B^{N_B}\ldots\vartheta^E$ is the number of accessible complexions of this phase when it has energy $E$, and numbers of system $N_A, N_B, \ldots$, due regard being paid to symmetry requirements. The function $\Xi$ itself is therefore the sum of $\lambda_A^{N_A}\lambda_B^{N_B}\ldots\vartheta^E$ over all complexions for all values of the energy $E$ and all values of the numbers of systems $N_A, N_B, \ldots$. It is precisely the function which we have already agreed to call the grand partition function for this phase. It follows from the method of construction of $\Xi$, which we have just described, that the frequency of occurrence of any particular set of conditions in the phase is proportional to the sum of the terms in $\Xi$ which satisfy this set of conditions. In particular if any property has the value $Q$ in a set of terms $\delta\Xi$ of $\Xi$, then

its average value $\bar{Q}$ in the phase for given $T$, $V$, $\lambda_A$, $\lambda_B$, ... is given by

$$\bar{Q} = \Sigma\, Q\delta\Xi/\Xi. \qquad (602, 7)$$

Although we have given a detailed proof of the relation (5) between the thermodynamic potential $Xx(T, V, \mu)$ and the grand partition function $\Xi(\vartheta, V, \lambda)$ only for the case of a single gaseous phase, the relation is perfectly general, provided $\Xi$ is constructed as the polynomial in $\lambda_A, \lambda_B, \ldots, \vartheta$ such that the coefficient of $\lambda_A^{N_A}\lambda_B^{N_B}\ldots\vartheta^E$ is the number of accessible complexions of the whole assembly when it has energy $E$, and numbers of systems $N_A, N_B, \ldots$, due regard being paid to symmetry requirements. In particular one can verify that the grand partition function $\Xi$ for an assembly of several phases will be the product of the $\Xi$'s for each phase. This leads to the required additivity properties for the several phases.

Let us consider for example an assembly consisting of two phases, and let us denote the properties of the phases by symbols with a single prime and a double prime respectively. Then

$$\Xi = \Xi'\Xi''. \qquad (602, 8)$$

By the method of § 215 one can then show that the average number of systems of type $A$ in each phase are given by

$$N'_A = \lambda_A \frac{\partial \log \Xi'}{\partial \lambda_A}, \quad N''_A = \lambda_A \frac{\partial \log \Xi''}{\partial \lambda_A}. \qquad (602, 9)$$

From (2) and (5) we see that the relations (9) are equivalent to

$$N'_A = \frac{\partial (Xx)'}{\partial \mu_A}, \quad N''_A = -\frac{\partial (Xx)''}{\partial \mu_A}, \qquad (602, 10)$$

which is just the thermodynamic formula (601, 11) generalized to two phases.

We may note further, since $x$ is the only extensive variable in $\Xi$ (i.e the only variable whose value increases proportionally to the amount of the phase), that for each phase $\Xi$ must be of the form

$$\Xi(\vartheta, x, \lambda_A, \lambda_B, \ldots) = [\Xi(\vartheta, \lambda_A, \lambda_B, \ldots)]^x, \qquad (602, 11)$$

or

$$\log \Xi(\vartheta, x, \lambda_A, \lambda_B, \ldots) = x \log \Xi(\vartheta, \lambda_A, \lambda_B, \ldots), \qquad (602, 12)$$

where $\Xi$ is independent of $x$, that is to say independent of the extent of the phase. By using (601, 10) and (5) we derive for the generalized force

$$X = kT\frac{\partial \log \Xi}{\partial x} = kT\frac{\log \Xi}{x} = kT \log \Xi(\vartheta, \lambda_A, \lambda_B, \ldots). \qquad (602, 13)$$

Formulae (9) and (13) are the statistical transcriptions of the thermodynamic formulae (601, 10) and (601, 11). We have still to derive the

statistical equivalent of (601, 9). We have

$$\left(\frac{\partial[Xx]}{\partial T}\right)_{x,\lambda} = \left[\left(\frac{\partial}{\partial T}\right)_{x,\mu} + \Sigma_A \left(\frac{\partial \mu_A}{\partial T}\right)_{x,\lambda} \left(\frac{\partial}{\partial \mu_A}\right)_{T,x}\right](Xx)$$
$$= \left[\left(\frac{\partial}{\partial T}\right)_{x,\mu} + \Sigma_A \frac{\mu_A}{T} \left(\frac{\partial}{\partial \mu_A}\right)_{T,x}\right](Xx)$$
$$= S + \frac{\Sigma_A N_A \mu_A}{T} = \frac{E + Xx}{T}, \qquad (602, 14)$$

using (2), (601, 9), (601, 11) and (601, 7). Combining (5) with (14) we obtain

$$kT^2\left(\frac{\partial \log \Xi}{\partial T}\right)_{x,\lambda} = T^2\left(\frac{\partial}{\partial T}\frac{Xx}{T}\right)_{x,\lambda} = T\left(\frac{\partial}{\partial T}Xx\right)_{x,\lambda} - Xx = E. \quad (602, 15)$$

In most applications it will be allowable to use the approximations of classical statistics, for which the necessary conditions are that $\lambda_A \ll 1$ for all types of systems. We can then replace (3) by the approximation

$$Xx = kT \log \Xi = kT\,\Sigma_A\, \lambda_A\, \Sigma_r\, \varpi_r e^{-\epsilon_r/kT} = kT\,\Sigma_A\, \lambda_A f_A(T), \quad (602, 16)$$

where $f_A(T)$ is the ordinary partition function for a system of type $A$. We shall apply these results in the following sections. Before doing so, however, it is interesting to record how (16) may be obtained directly, without proceeding via quantum statistics. If the partition function for a single free system of type $A$ in volume $V$ is $f_A(T)$, the partition function for $N_A$ systems would be $\{f_A(T)\}^{N_A}$, except that in integrating or summing over all $V$ for each of the $N_A$ systems independently one permutes all the $N_A$ systems completely. Every distinct state of the assembly is thus counted $N_A!$ times, and the correct assembly partition function for $N_A$ free systems must be

$$\{f_A(T)\}^{N_A}/N_A!. \qquad (602, 17)$$

When there are several types of systems this can be generalized at once to

$$\{f_A(T)\}^{N_A}\{f_B(T)\}^{N_B}\ldots/N_A!\,N_B!\ldots. \qquad (602, 18)$$

The grand partition function is therefore given by

$$\Xi = \Sigma_A\, \Sigma_B \ldots \lambda_A^{N_A} \lambda_B^{N_B} \ldots \{f_A(T)\}^{N_A}\{f_B(T)\}^{N_B}\ldots/N_A!\,N_B!\ldots, \quad (602, 19)$$

or

$$\Xi = e^{\lambda_A f_A(T) + \lambda_B f_B(T) + \ldots}. \qquad (602, 20)$$

On taking logarithms and multiplying by $kT$ we recover (16).

**§ 603. Use of the grand partition function for a gaseous phase.** We shall now verify directly that the use of the grand partition function leads to all the usual results when applied to a perfect gas.

We have already in § 219 enumerated the quantal states of structureless particles in a rectangular enclosure. According to (219, 2) the possible

energies of structureless particles $A$ of mass $m_A$ in a rectangular enclosure with sides of length $a$, $b$, $c$ are given by

$$\epsilon_{l,m,n} = \frac{h^2}{8m_A}\left(\frac{l^2}{a^2}+\frac{m^2}{b^2}+\frac{n^2}{c^2}\right) \quad (l, m, n = 1, 2, \ldots). \qquad (603, 1)$$

Since therefore for a given energy $\epsilon$

$$\frac{l^2}{a^2}+\frac{m^2}{b^2}+\frac{n^2}{c^2} = \frac{8m_A}{h^2}\epsilon, \qquad (603, 2)$$

the number of states of translational kinetic energy less than or equal to $\epsilon$ is equal to the volume of an octant of the ellipsoid (2) in $l$, $m$, $n$ space. This ellipsoid has semi-axes $a(8m_A\epsilon)^{\frac{1}{2}}/h$, $b(8m_A\epsilon)^{\frac{1}{2}}/h$, $c(8m_A\epsilon)^{\frac{1}{2}}/h$ and the volume of an octant is therefore

$$\frac{1}{8}\frac{4\pi}{3}\frac{(8m_A\epsilon)^{\frac{3}{2}}}{h^3}abc = \frac{4\pi}{3}\frac{(2m_A)^{\frac{3}{2}}}{h^3}V\epsilon^{\frac{3}{2}}, \qquad (603, 3)$$

where $V$ denotes the volume of the enclosure. It can be shown that this number is independent of the shape of the enclosure as soon as it is reasonably large. If instead of structureless particles we consider systems with internal structure, but with their internal degrees of freedom completely unexcited, each translational energy state will have a weight $\varpi_A$ and we should then replace (3) by

$$\frac{4\pi}{3}\varpi_A\frac{(2m_A)^{\frac{3}{2}}}{h^3}V\epsilon^{\frac{3}{2}}. \qquad (603, 4)$$

By differentiation of (4) we find for the number of states in the energy range $\epsilon$, $\epsilon+d\epsilon$

$$2\pi\varpi_A\frac{(2m_A)^{\frac{3}{2}}}{h^3}V\epsilon^{\frac{1}{2}}d\epsilon. \qquad (603, 5)$$

The grand partition function $\Xi$ is therefore given, according to (602, 6) for one type of system, by

$$\log\Xi = 2\pi\varpi_A\frac{(2m_A)^{\frac{3}{2}}}{h^3}V\int_0^\infty \epsilon^{\frac{1}{2}}\log(1\pm\lambda_A e^{-\epsilon/kT})^{\pm 1}d\epsilon. \qquad (603, 6)$$

For the assembly here considered the geometrical coordinate $x$ is the volume $V$, and the corresponding generalized force $X$ the pressure $P$. Hence by (602, 5)

$$PV = kT\log\Xi = 2\pi\varpi_A kT\frac{(2m_A)^{\frac{3}{2}}}{h^3}V\int_0^\infty \epsilon^{\frac{1}{2}}\log(1\pm\lambda_A e^{-\epsilon/kT})^{\pm 1}d\epsilon. \quad (603, 7)$$

By integration by parts we can transform (7) to

$$PV = 2\pi\varpi_A\frac{(2m_A)^{\frac{3}{2}}}{h^3}V\int_0^\infty \frac{\frac{2}{3}\epsilon^{\frac{3}{2}}d\epsilon}{e^{\epsilon/kT}/\lambda_A \pm 1}. \qquad (603, 8)$$

On changing the variable of integration by putting $\epsilon/kT = y$, we find

$$PV = 2\pi\varpi_A \frac{(2m_A)^{\frac{3}{2}}(kT)^{\frac{5}{2}}}{h^3} \int_0^\infty \frac{\frac{2}{3}y^{\frac{3}{2}}dy}{e^y/\lambda_A \pm 1}. \tag{603, 9}$$

The average (kinetic) energy can be most readily derived from (9) by using (602, 15). We have

$$E = kT^2\left(\frac{\partial}{\partial T}\left[\frac{PV}{kT}\right]\right)_{V,\lambda_A} = \tfrac{3}{2}PV. \tag{603, 10}$$

This relationship can also be derived from an expression for the average number of systems in states in the energy range $\epsilon$, $\epsilon+d\epsilon$ which is frequently useful. This number is according to (217, 1) equal to the number (5) of states in this range multiplied by the factor $(e^{\epsilon/kT}/\lambda_A \pm 1)^{-1}$, that is

$$2\pi\varpi_A \frac{(2m_A)^{\frac{3}{2}}}{h^3} V \frac{\epsilon^{\frac{1}{2}}d\epsilon}{e^{\epsilon/kT}/\lambda_A \pm 1}. \tag{603, 11}$$

Each of these systems has kinetic energy $\epsilon$. On multiplying (11) by $\epsilon$ and integrating we obtain the expression (8) without the factor $\frac{2}{3}$, in agreement with (10).

In deriving (10) we have not restricted the value of $\lambda_A$. We have already derived (10) in Chapter III for a classical gas ($\lambda_A \ll 1$), but we now see that the formula is equally valid for all values of $\lambda_A$. In the discussion of free electrons in metals in Chapter XI we shall have an example of the opposite case, $\lambda_A \gg 1$, when the relation (10) will still hold.

In deriving (10) here we have allowed the systems to have a weight factor $\varpi_A$ due to their internal structure, but no excited states. This restriction is unnecessary. For if we group together all the systems in a particular internal state we can derive a relation such as (10) for the particular group, and then by summation over all groups extend it to the whole assembly. It will be observed that the numerical factor $\frac{3}{2}$ in (10) is determined entirely by the distribution of the energies, being such that the number of states in the range $\epsilon$, $\epsilon+d\epsilon$ is proportional to $\epsilon^{\frac{1}{2}}d\epsilon$. One can verify generally that if the number of states of energy in the range $\epsilon$, $\epsilon+d\epsilon$ is proportional to $\epsilon^r d\epsilon$ then

$$E = (r+1)PV. \tag{603, 12}$$

By applying the standard formula (601, 11) to (7) we find here

$$N_A = \frac{\partial(PV)}{\partial\mu_A} = \frac{\lambda_A}{kT}\frac{\partial(PV)}{\partial\lambda_A} = 2\pi\varpi_A \frac{(2m_A)^{\frac{3}{2}}}{h^3} V \int_0^\infty \frac{\epsilon^{\frac{1}{2}}d\epsilon}{e^{\epsilon/kT}/\lambda_A \pm 1}, \tag{603, 13}$$

which is the form taken by (216, 3) for an assembly of free systems in an enclosure.

Under the conditions for classical statistics ($\lambda_A \ll 1$), we can omit the $\pm 1$ in the denominators of such formulae as (8) and (13) and can then eliminate

$\lambda_A$ by dividing the one by the other. We thus recover the formula

$$\frac{PV}{N_A} = \frac{\int_0^\infty \tfrac{2}{3}\epsilon^{\frac{3}{2}} e^{-\epsilon/kT}\,d\epsilon}{\int_0^\infty \epsilon^{\frac{1}{2}} e^{-\epsilon/kT}\,d\epsilon} = kT, \tag{603, 14}$$

by integration by parts of the numerator. This classical result can be derived in other ways from the grand partition function. If we use directly the classical approximation (602, 20) for the grand partition function of a mixture of perfect gases, we have

$$PV = kT\log \Xi = kT\,\Sigma_A\,\lambda_A f_A(T). \tag{603, 15}$$

From this we have
$$N_A = \frac{\lambda_A}{kT}\frac{\partial(PV)}{\partial\lambda_A} = \lambda_A f_A(T). \tag{603, 16}$$

Thus by comparison of (15) and (16)

$$PV = \Sigma_A\,N_A kT, \tag{603, 17}$$

or in the case of a single type of system

$$PV = N_A kT, \tag{603, 18}$$

agreeing with (14). From (16) we also derive

$$\mu_A = kT\log\lambda_A = kT\log\{N_A/f_A(T)\}, \tag{603, 19}$$

in agreement with (225, 5) for any classical gaseous assembly.

**§ 604. A two-dimensional gas.** Relations analogous to those of § 603 can be obtained for an assembly of systems completely free to move on a surface, but without freedom normal to it. Such an idealized assembly is a fair representation of certain types of adsorbed films.* The treatment is so similar to that of a three-dimensional gas that it can be briefly summarized. The number of states with energy less than $\epsilon$ is now given by the area of a quadrant of the ellipse

$$\frac{l^2}{a^2}+\frac{m^2}{b^2} = \frac{8m_A}{h^2}\epsilon, \tag{604, 1}$$

and this is equal to

$$\tfrac{1}{4}\pi\,\frac{(8m_A\epsilon)^{\frac{1}{2}}a}{h}\,\frac{(8m_A\epsilon)^{\frac{1}{2}}b}{h} = \frac{2\pi m_A}{h^2}A\epsilon, \tag{604, 2}$$

where $A$ is the area of the surface accessible to the adsorbed systems. The number of states in the range $\epsilon$, $\epsilon+d\epsilon$ is therefore

$$\frac{2\pi m_A}{h^2}A\,d\epsilon, \tag{604, 3}$$

* See for example Adam, *Physics and Chemistry of Surfaces*, Ed. 2, p. 40 (Oxford, 1938).

the coefficient of $d\epsilon$ being in this case independent of $\epsilon$. Hence on applying (603, 12) we find for the translational kinetic energy

$$E^{\text{kin}} = \phi A, \tag{604, 4}$$

where $\phi$ is the two-dimensional pressure or spreading force per unit length of boundary. The analogues of (603, 8) and (603, 13) are

$$\phi A = \frac{2\pi\varpi_A m_A}{h^2} A \int_0^\infty \frac{\epsilon\, d\epsilon}{e^{\epsilon/kT}/\lambda_A \pm 1}, \tag{604, 5}$$

$$N_A = \frac{2\pi\varpi_A m_A}{h^2} A \int_0^\infty \frac{d\epsilon}{e^{\epsilon/kT}/\lambda_A \pm 1}. \tag{604, 6}$$

In the classical case ($\lambda_A \ll 1$) we can omit the $\pm 1$ in the denominators of (5) and (6), and then obtain directly by division

$$\frac{\phi A}{N_A} = \frac{\int_0^\infty \epsilon e^{-\epsilon/kT}\, d\epsilon}{\int_0^\infty e^{-\epsilon/kT}\, d\epsilon} = kT. \tag{604, 7}$$

**§ 605. Crystals of a single component.** In constructing the partition function $f(T)$ for a molecule of gas or the grand partition function $\Xi$ for the complete gaseous phase, we have found it natural to construct them for a given volume of the phase, a volume which is entirely independent of the number of molecules in the phase. In this way one constructs the functions $f(T, V)$ and $\Xi(T, V, \lambda)$ as functions of the variables specified and of no others. In the elementary discussion of crystals, however, given in Chapter IV, we have allowed the volume of the crystal to be fixed by or to fix the number of molecules it contains. This is a physically proper approximation, owing to the small compressibility of a crystalline solid. If, however, we wish, as we now do, to construct the grand partition function $\Xi$ for a crystal, it is essential not to make this approximation, for it is essential that the theoretical independence of $V$ and $N$ should be preserved, or the analysis cannot be carried through. We therefore must and can only aim at constructing a grand partition function $\Xi$ for a crystal, which takes explicit account of the fact that a crystal is compressible, and that $V$ and $N$ are not uniquely determined the one by the other.

We proceed therefore as follows. We consider a crystal of given lattice structure occupying a given volume $V$, but of at present undetermined lattice constant or scale, so that it may contain any number of molecules. Actually, only lattice constants very near the natural one will matter, so that errors in the energy states used for widely divergent lattice constants,

which are either very large or very small, are not of any serious moment. For each choice of lattice constant, and therefore of $N$, we may suppose that we can construct an ordinary crystal partition function as in Chapter IV, which will be of the form $\{\kappa(T)\}^N$, or more precisely

$$\{\kappa(T, V/N)\}^N. \qquad (605, 1)$$

We assume that the change of scale is sufficiently isotropic to be adequately represented by the single variable $V/N$. This partition function has the required property that the coefficient of $e^{-E/kT}$, in its expansion as a series of powers of $\vartheta = e^{-1/kT}$, is the number of complexions of the crystal with energy $E$. Provided that we can construct (1) adequately, we can construct the required grand partition function in the form

$$\Xi = \Sigma_N \lambda^N\{\kappa(T, V/N)\}^N. \qquad (605, 2)$$

For brevity we write (2) as

$$\Xi = \Sigma_N \Xi_N(T, V/N), \qquad (605, 3)$$

where

$$\Xi_N = \lambda^N\{\kappa(T, V/N)\}^N. \qquad (605, 4)$$

Owing to the occurrence of $N$ in the argument $V/N$, the series (3) cannot be summed explicitly. It can, however, be shown that, under suitable conditions always satisfied in practice, $\Xi_N$ has a unique maximum $\Xi_{N^*}$ for some value $N^*$ of $N$, and that we may then use the approximation

$$\log \Xi \simeq \log \Xi_{N^*}. \qquad (605, 5)$$

This means that all the average properties of the crystal can be derived by replacing the series $\Xi$ by the single term for $N = N^*$, where $N^*$ satisfies the relation

$$\frac{\partial \log \Xi_N}{\partial N} = 0 \quad (N = N^*). \qquad (605, 6)$$

Owing to this relation we can treat $N^*$ as a constant whenever we differentiate $\Xi_{N^*}$ with respect to $T$ or $V$ or $\lambda$, although $N^*$ is actually a function of $T$, $V$, $\lambda$. For the average value of $N$ we thus obtain, by (602, 9) and (4),

$$\overline{N} = \lambda \frac{\partial}{\partial \lambda} \log \Xi_{N^*} = \lambda \frac{\partial}{\partial \lambda} \log\{\lambda^{N^*}[\kappa(T, V/N)]^{N^*}\} = N^*. \qquad (605, 7)$$

Having established the equality of $\overline{N}$ and $N^*$ we need no longer distinguish between them.

According to the definition (4) of $\Xi_N$, equation (6) becomes

$$\frac{\partial}{\partial N}[N \log \lambda + N \log \kappa(T, V/N)] = 0 \quad (N = \overline{N}), \qquad (605, 8)$$

or

$$\log \lambda + \log \kappa(T, V/N) + N \frac{\partial \log \kappa(T, V/N)}{\partial N} = 0 \quad (N = \overline{N}). \qquad (605, 9)$$

If, as usual, we denote the average molecular volume $V/\bar{N}$ by $v$, we can write (9) as

$$\log\lambda + \log\kappa(T, v) - v\frac{\partial \log\kappa(T, v)}{\partial v} = 0. \qquad (605, 10)$$

Since in the present example the geometrical variable $x$ is the volume $V$, the corresponding generalized force is the pressure $P$. We have therefore by (602, 13)

$$P = kT\frac{\partial \log \Xi}{\partial V} = kT\frac{\partial \log \Xi_{N^*}}{\partial V}$$

$$= N^*kT\frac{\partial \log\kappa(T, V/N^*)}{\partial V} = kT\frac{\partial \log\kappa(T, v)}{\partial v}. \qquad (605, 11)$$

In operating with $\partial/\partial V$ in (11) we again treat $N^*$ as a constant, since by its definition $\partial\Xi_{N^*}/\partial N^*$ vanishes.

If we substitute from (11) into (10), we obtain

$$\log\lambda = -\log\kappa + Pv/kT, \qquad (605, 12)$$

or according to (602, 2) $\quad \mu = -kT\log\kappa + Pv. \qquad (605, 13)$

The molecular free energy $F$ is accordingly given by

$$F = \mu - Pv = -kT\log\kappa. \qquad (605, 14)$$

Formulae (13) and (14) are identical with the formulae used already in Chapters IV and V. We notice that (12) can be rewritten

$$PV = kT\log(\lambda\kappa)^{N^*} = kT\log\Xi_{N^*}, \qquad (605, 15)$$

which is effectively equivalent to the general relation

$$PV = kT\log\Xi. \qquad (605, 16)$$

**§ 606. Perfect mixed crystals.** The results of § 605 can be extended to the simplest type of mixed crystal. The partition function for a mixed crystal of volume $V$ containing $N_A$ molecules $A$ and $N_B$ molecules $B$, where $N_A + N_B = N$, in a *given configuration* can always be written formally as $[\kappa_A(T, V/N)]^{N_A}[\kappa_B(T, V/N)]^{N_B}$, but this expression is useful only if both $\kappa_A$ and $\kappa_B$ are really independent of the ratio $N_A/N_B$ and of the actual configuration of the two different types of molecule on the $N$ lattice points. If we assume that $\kappa_A$ and $\kappa_B$ are independent of this ratio, they may then be taken to be of the forms

$$\kappa_A(T, V/N) = \alpha(T, V/N)\, j_A(T)\, e^{\chi_A(T,V/N)/kT}, \qquad (606, 1)$$

$$\kappa_B(T, V/N) = \alpha(T, V/N)\, j_B(T)\, e^{\chi_B(T,V/N)/kT}, \qquad (606, 2)$$

where the partition function $\alpha(T, V/N)$ for the acoustical modes, the partition functions $j_A(T)$, $j_B(T)$ for the internal degrees of freedom of each type of molecule, and the energies $-\chi_A$, $-\chi_B$ of the two types in their

lowest energy states in the crystal (relative to an energy zero at complete dispersion in a gaseous phase in their lowest possible states) are all independent of the ratio $N_A/N_B$, and of the actual configuration on the lattice points. When all these conditions are fulfilled we call the mixed crystal *perfect*.

We can now form the grand partition function. The ordinary partition function for a crystal of $N_A$ and $N_B$ systems *including all configurations on the lattice points* is

$$\frac{N!}{N_A!\,N_B!}\{\kappa_A(T, V/N)\}^{N_A}\{\kappa_B(T, V/N)\}^{N_B} \quad (N_A+N_B=N). \qquad (606, 3)$$

The grand partition function is therefore

$$\Xi = \Sigma_{N_A}\Sigma_{N_B}\frac{(N_A+N_B)!}{N_A!\,N_B!}\lambda_A^{N_A}\lambda_B^{N_B}\{\kappa_A(T, V/N)\}^{N_A}\{\kappa_B(T, V/N)\}^{N_B}. \quad (606, 4)$$

This double series can be partially summed by grouping together the terms of given $N$. We thus obtain

$$\Xi = \Sigma_N[\lambda_A\kappa_A(T, V/N)+\lambda_B\kappa_B(T, V/N)]^N. \qquad (606, 5)$$

Just as for the crystal of a single component we may with sufficient accuracy replace the series $\Xi$ by its maximum term $\Xi_{N^*}$, so that

$$\log\Xi \simeq \log\Xi_{N^*} = N^*\log\{\lambda_A\kappa_A(T, V/N^*)+\lambda_B\kappa(T, V/N^*)\}, \quad (606, 6)$$

where $N^*$ is determined by

$$\frac{\partial\log\Xi_N}{\partial N} = 0 \quad (N=N^*), \qquad (606, 7)$$

and consequently we may treat $N^*$ as a constant whenever we differentiate $\Xi_{N^*}$ with respect to $T$, $V$, $\lambda_A$ or $\lambda_B$, although $N^*$ in fact depends on these variables.

For the average number of molecules of the two types in the crystal we have by (602, 9)

$$\overline{N_A} = \lambda_A\frac{\partial}{\partial\lambda_A}\log\Xi = \lambda_A\frac{\partial}{\partial\lambda_A}\log\Xi_{N^*} = N^*\frac{\lambda_A\kappa_A}{\lambda_A\kappa_A+\lambda_B\kappa_B}, \quad (606, 8)$$

and similarly

$$\overline{N_B} = N^*\frac{\lambda_B\kappa_B}{\lambda_A\kappa_A+\lambda_B\kappa_B}. \qquad (606, 9)$$

When we add these two equations we obtain

$$\overline{N} = \overline{N_A}+\overline{N_B} = N^*, \qquad (606, 10)$$

and consequently we need no longer distinguish between $N^*$ and $\overline{N}$.

The pressure $P$ is according to (602, 5) given by

$$PV = kT\log\Xi = kT\log\Xi_{N^*} = NkT\log(\lambda_A\kappa_A+\lambda_B\kappa_B). \quad (606, 11)$$

If we denote the molecular volume by $\mathrm{v} = V/N$, we can write this as

$$P\mathrm{v} = kT\log(\lambda_A\kappa_A + \lambda_B\kappa_B). \qquad (606, 12)$$

Alternatively we have using (602, 13)

$$P = N^*kT\frac{\partial}{\partial V}\log[\lambda_A\kappa_A(T, V/N^*) + \lambda_B\kappa_B(T, V/N^*)]$$

$$= kT\frac{\partial}{\partial \mathrm{v}}\log[\lambda_A\kappa_A(T, \mathrm{v}) + \lambda_B\kappa_B(T, \mathrm{v})]. \qquad (606, 13)$$

The mutual consistency of (12) and (13) follows from (7) which can be rewritten as

$$\log(\lambda_A\kappa_A + \lambda_B\kappa_B) - \mathrm{v}\frac{\partial}{\partial \mathrm{v}}\log(\lambda_A\kappa_A + \lambda_B\kappa_B) = 0. \qquad (606, 14)$$

By combining (12) with (8) we can obtain

$$\lambda_A = \frac{\overline{N_A}}{N}\frac{1}{\kappa_A}e^{P\mathrm{v}/kT}, \quad \lambda_B = \frac{\overline{N_B}}{N}\frac{1}{\kappa_B}e^{P\mathrm{v}/kT}. \qquad (606, 15)$$

These relations are readily extended to perfect mixed crystals of more than two components, and may be expressed in words as follows: *In perfect mixed crystals at given temperature and pressure the absolute activity $\lambda_A$ of each molecular species A is directly proportional to its molecular fraction $N_A/N$.*

**§ 607. Ideal assemblies and regular assemblies.** The results which we have so far obtained in this chapter merely repeat results that we had previously obtained by less elaborate and more familiar methods. The real utility of grand partitions appears only when they are applied to assemblies less simple than those discussed hitherto. In particular they are useful in the treatment of certain *cooperative* assemblies which may be called *regular* assemblies. We now proceed to explain what we mean by *cooperative* and by *regular*.

We can conveniently divide assemblies into classes, according to the degree of interaction between the systems (molecules, atoms, electrons, ions) of which they are composed. When such interaction is negligible we call the assembly *ideal*; the obvious example is a perfect gas, or mixture of perfect gases, discussed in Chapter III; another example will be found in § 823 where an extremely dilute solution of a non-electrolyte is treated as an ideal assembly of the solute species. When the interaction is not negligible, but still small, we have a *slightly non-ideal assembly*; important examples are slightly imperfect gases discussed in Chapter VII, and extremely dilute solutions of electrolytes discussed in Chapter IX. When on the other hand the interactions are so important that the states of any distinct system are fundamentally influenced by which states of the other systems are occupied,

it becomes practically impossible to treat the constituent systems as almost independent. Under these conditions the assembly is called *cooperative*. The application of statistical mechanics to cooperative assemblies is considerably more difficult than to ideal or slightly non-ideal assemblies, and usually special devices are required. We have already met one example of such devices. A crystal regarded as an assembly of atoms or molecules is a cooperative assembly, but in Chapter IV we were able to use the methods applicable to ideal assemblies by the device of treating the normal modes of vibration of the crystal as an ideal assembly of oscillators.

The considerable advances, made recently and described in Chapter VIII, in the application of statistical mechanics to liquids have depended on the realization that a liquid is a cooperative assembly, and earlier discussions involved an altogether unjustifiable extrapolation of results, derived only for slightly imperfect gases. Another important example of a cooperative assembly is a ferromagnetic substance; the subject of ferromagnetism will be briefly discussed in Chapter XIV. At this stage we wish to consider a specially simple kind of cooperative assembly, which we shall call a *regular* assembly. This name seems appropriate because a typical example of such an assembly is a *regular solution*, a name due to Hildebrand,* and used in a slightly altered sense in Chapter VIII.

We now define a *regular* assembly as a cooperative assembly with the following properties:

(1) Any configuration of the assembly can be described by specifying the number and geometry of occupiable sites in the assembly and how each site is occupied.

(2) Interactions between pairs of molecules that are not nearest neighbours may be neglected, and therefore the interaction energy of the systems composing the assembly can for each configuration be expressed as the sum of contributions from each pair of immediate neighbours.

(3) The internal degrees of freedom of each system are independent of its neighbours.

In the following section we shall describe a general method for obtaining an approximate evaluation of the grand partition function for regular assemblies. We shall later repeat the treatment in detail for various examples of regular assemblies as these occur. In particular we shall apply the method to regular solutions in § 820, to regular monolayers in § 1011, and to a solution of atomic hydrogen in palladium in § 1309. The method of the following section will be extended in Chapter XIII so as to apply to alloys with a super-lattice structure.

* Hildebrand, *J. Am. Chem. Soc.* 51, 66 (1929).

In two of these examples of regular assemblies, namely solutions of hydrogen in palladium and monolayers adsorbed on a crystalline surface, any site may be either empty or full. In a regular solution, on the other hand, every site must be occupied by a molecule of some kind. The distinction is, however, irrelevant for what follows.

**§ 608. Grand partition function for a regular assembly.** We now describe a procedure* for evaluating approximately the grand partition function of a regular assembly. We denote by $N$ the total number of sites, by $N_\alpha$ the number occupied *in the manner* $\alpha$, by $N_\beta$ the number occupied *in the manner* $\beta$, and so on. Of the quantities $N_\alpha, N_\beta, \ldots$ we could define at least all but one of them by saying that $N_\alpha$ denotes the number of sites occupied *by systems of type* $\alpha$, and so on. But there may be one quantity of the set $N_\alpha, N_\beta, \ldots$, say $N_0$, which denotes the number of empty sites. In this case occupied *in the manner* 0 means *empty*, but occupied in any other manner $\alpha, \beta, \ldots$ means occupied by systems of the type $\alpha, \beta, \ldots$. We further denote by $N_{\alpha\beta}$ the number of pairs of neighbouring sites the one occupied in the manner $\alpha$ and the other in the manner $\beta$. We denote by $z$ the number of closest neighbours of each site. For liquids the number of closest neighbours fluctuates slightly and $z$ must be regarded as the average value; for all the other examples $z$ is a true constant determined by the type of lattice. We have then the necessary equalities

$$\Sigma_\alpha N_\alpha = N, \tag{608, 1}$$

$$2N_{\alpha\alpha} + \sum_{\alpha \neq \beta} N_{\alpha\beta} = zN_\alpha \quad \text{or} \quad \Sigma_\beta \sigma_{\alpha\beta} N_{\alpha\beta} = zN_\alpha, \tag{608, 2}$$

where $\sigma_{\alpha\beta}$ is the usual symmetry number equal to 2 when $\alpha$ and $\beta$ are identical and equal to 1 otherwise.

The grand partition function $\Xi$ for an assembly with $N$ sites is then defined by

$$\Xi = \sum_{N_\alpha, \ldots} \sum_{N_{\alpha\beta}, \ldots} g(N_\alpha, \ldots, N_{\alpha\beta}, \ldots)\, e^{-\Sigma N_{\alpha\beta} w_{\alpha\beta}/kT} (\lambda_\alpha \phi_\alpha)^{N_\alpha} (\lambda_\beta \phi_\beta)^{N_\beta}, \tag{608, 3}$$

where $g(N_\alpha, \ldots, N_{\alpha\beta}, \ldots)$ denotes the number of distinguishable configurations for the specified values of $N_\alpha, \ldots, N_{\alpha\beta}, \ldots$. The contribution of each $\alpha\beta$ pair of neighbours to the interaction energy is denoted by $w_{\alpha\beta}$. The partition function of a system $\alpha$ for all degrees of freedom, and all forms of energy other than the interaction energy, is denoted by $\phi_\alpha$. We can, if we wish, include in each of $\phi_\alpha, \phi_\beta, \ldots$ an extra factor so that $w_{\alpha\alpha}, w_{\beta\beta}, \ldots$ become zero, and $w_{\alpha\beta}$ becomes the excess energy of an $\alpha\beta$ pair over the mean of the

* Guggenheim, *Proc. Roy. Soc.* A, **169**, 134 (1938). The method used is a variant of that invented by Bethe, *Proc. Roy. Soc.* A, **150**, 552 (1935), and adapted by Peierls, *Proc. Camb. Phil. Soc.* **32**, 471 (1936).

energies of an $\alpha\alpha$ pair and a $\beta\beta$ pair. This is, however, merely a matter of convenience and is irrelevant to our further procedure. Finally $\lambda_\alpha, \lambda_\beta, \ldots$ denote, as usual, the absolute activities of $\alpha, \beta, \ldots$. For an unoccupied site the analogous quantities $\lambda_0$ and $\phi_0$ are unity.

For the given values of $T$, $\lambda_\alpha, \lambda_\beta, \ldots$ the frequency of occurrence of a configuration of specified $N_\alpha, N_\beta, \ldots$ and $N_{\alpha\beta}, \ldots$ is proportional to the term in $\Xi$ with these values of $N_\alpha, N_\beta, \ldots$ and $N_{\alpha\beta}, \ldots$. We have as usual

$$\overline{N_\alpha} = \lambda_\alpha \frac{\partial \log \Xi}{\partial \lambda_\alpha}, \tag{608, 4}$$

and it follows from (602, 7) that

$$\overline{N_{\alpha\beta}} = -kT \frac{\partial \log \Xi}{\partial w_{\alpha\beta}}. \tag{608, 5}$$

For brevity's sake it is convenient to introduce the quantities $\xi_\alpha, \xi_\beta, \ldots$ and $\eta_{\alpha\beta}, \ldots$ defined by

$$\xi_\alpha = \lambda_\alpha \phi_\alpha, \tag{608, 6}$$

$$\eta_{\alpha\beta} = e^{-w_{\alpha\beta}/kT}. \tag{608, 7}$$

The formula for $\Xi$ now becomes

$$\Xi = \sum_{N_\alpha, \ldots} \sum_{N_{\alpha\beta}, \ldots} g(N_\alpha, \ldots, N_{\alpha\beta}, \ldots)\, \eta_{\alpha\beta}^{N_{\alpha\beta}} \ldots \xi_\alpha^{N_\alpha} \xi_\beta^{N_\beta} \ldots, \tag{608, 8}$$

and the relations (4) and (5) become

$$\overline{N_\alpha} = \xi_\alpha \frac{\partial \log \Xi}{\partial \xi_\alpha}, \tag{608, 9}$$

$$\overline{N_{\alpha\beta}} = \eta_{\alpha\beta} \frac{\partial \log \Xi}{\partial \eta_{\alpha\beta}}. \tag{608, 10}$$

In deriving averages the error can, as usual, be shown to be negligible if one replaces the series for $\Xi$ by its greatest term. If this term is $\Xi_{(N^*)}$, say, defined by

$$\Xi_{(N^*)} = g(N^*_\alpha, \ldots, N^*_{\alpha\beta}, \ldots)\, \eta_{\alpha\beta}^{N^*_{\alpha\beta}} \ldots \xi_\alpha^{N^*_\alpha} \xi_\beta^{N^*_\beta} \ldots, \tag{608, 11}$$

then the average values of $N_\alpha, N_\beta, \ldots$ and $N_{\alpha\beta}, \ldots$ are given by

$$\overline{N_\alpha} = N^*_\alpha, \quad \overline{N_{\alpha\beta}} = N^*_{\alpha\beta}. \tag{608, 12}$$

These values may be determined approximately by a special device.

We define the quantities $\xi$, $\eta$, $\gamma$ by

$$\xi^N = \Pi_\alpha \xi_\alpha^{N^*_\alpha}, \tag{608, 13}$$

$$\eta^{\frac{1}{2}zN} = \Pi_{\alpha,\beta} \eta_{\alpha\beta}^{N^*_{\alpha\beta}}, \tag{608, 14}$$

$$\gamma^N = g(N^*_\alpha, \ldots, N^*_{\alpha\beta}, \ldots). \tag{608, 15}$$

Thus $\xi$ is the geometric mean of the factors of the type $\xi_\alpha, \xi_\beta, \ldots$ contributed by each site to $\Xi_{(N^*)}$; $\eta$ is the geometric mean of the factor of the type $\eta_{\alpha\beta}, \ldots$

contributed by each pair of neighbouring sites to $\Xi_{(N^\bullet)}$; $\gamma$ is the geometic mean of the factor contributed by each site to $g(N_\alpha^*, ..., N_{\alpha\beta}^*, ...)$. We also define $\eta_\alpha$ as the geometric mean of the factor of the type $\eta_{\alpha\beta}$ contributed to $\Xi_{(N^\bullet)}$ by each pair of neighbouring sites one of which is specified as being occupied in the manner $\alpha$.

Using these definitions we can express $\Xi_{(N^\bullet)}$ or $\Xi$ in a number of alternative forms, amongst which are

$$\Xi = \Xi_{(N^\bullet)} = \gamma^N \xi^N \eta^{\frac{1}{2}zN}, \tag{608, 16}$$

$$\Xi = \Xi_1 = (\Sigma_\alpha \xi_\alpha \eta_\alpha^z)\, \gamma^{N-1} \xi^{N-1} \eta^{\frac{1}{2}zN-z}, \tag{608, 17}$$

$$\Xi = \Xi_2 = (\Sigma_\alpha \Sigma_\beta \xi_\alpha \eta_\alpha^{z-1} \xi_\beta \eta_\beta^{z-1} \eta_{\alpha\beta})\, \gamma^{N-2} \xi^{N-2} \eta^{\frac{1}{2}zN-2z+1}, \tag{608, 18}$$

$$\Xi = \Xi_{z+1} = \Sigma_\alpha \xi_\alpha (\Sigma_\beta \xi_\beta \eta_\beta^{z-1} \eta_{\alpha\beta})^z\, \gamma^{N-z-1} \xi^{N-z-1} \eta^{\frac{1}{2}zN-z^2}. \tag{608, 19}$$

The form of $\Xi_1$ is such that the assembly is regarded as one site, which we may call the central state, and a residue, which forms an external field as far as the central site is concerned. The form of $\Xi_2$ is such that the assembly is regarded as a single pair of neighbouring sites, and a residue, which forms an external field as far as the single pair of neighbouring sites is concerned. The form of $\Xi_{z+1}$ is such that the assembly is regarded as a group of a central site and its $z$ neighbours, that is $z+1$ sites in all, and a residue

All the formulae (16) to (19) are merely formal, but valuable conclusions can be drawn from the assumption that they should lead to mutually consistent conclusions. In the first place the equality of the various forms for $\Xi$ requires that

$$\left.\begin{aligned} \Sigma_\beta \xi_\beta \eta_\beta^z &= \gamma \xi \eta^z, \\ \Sigma_\alpha \xi_\alpha \eta_\alpha^{z-1} \Sigma_\beta \xi_\beta \eta_\beta^{z-1} \eta_{\alpha\beta} &= \gamma^2 \xi^2 \eta^{2z-1} \\ \Sigma_\alpha \xi_\alpha (\Sigma_\beta \xi_\beta \eta_\beta^{z-1} \eta_{\alpha\beta})^z &= \gamma^{z+1} \xi^{z+1} \eta^{z^2}. \end{aligned}\right\} \tag{608, 20}$$

We can now derive alternative formulae for $\theta_\alpha$, the fraction of sites occupied in the manner $\alpha$, or the probability that a given site is occupied in the manner $\alpha$, by applying (9) either to $\Xi_1$ regarded as the $\Xi$ for a single site in a field due to the remaining sites, or to $\Xi_2$ regarded as the $\Xi$ for a pair of neighbouring sites in a field due to the remaining sites. We thus obtain on the one hand using (17)

$$\theta_\alpha = \frac{\overline{N_\alpha}}{N} = \xi_\alpha \frac{\partial \log \Xi_1}{\partial \xi_\alpha} = \frac{\xi_\alpha \eta_\alpha^z}{\gamma \xi \eta^z}, \tag{608, 21}$$

and on the other using (18)

$$\theta_\alpha = \frac{\overline{N_\alpha}}{N} = \tfrac{1}{2}\xi_\alpha \frac{\partial \log \Xi_2}{\partial \xi_\alpha} = \frac{\xi_\alpha \eta_\alpha^{z-1} \Sigma_\tau \xi_\tau \eta_\tau^{z-1} \eta_{\alpha\tau}}{\gamma^2 \xi^2 \eta^{2z-1}}. \tag{608, 22}$$

In order that (21) and (22) may be mutually consistent, we must have

$$\eta_\alpha = \frac{\Sigma_\tau \xi_\tau \eta_\tau^{z-1} \eta_{\alpha\tau}}{\gamma \xi \eta^{z-1}}, \tag{608, 23}$$

and this is also sufficient to ensure the satisfaction of the consistency of equations (20).

We might alternatively evaluate $\theta_\alpha$ from the relation

$$\theta_\alpha = \frac{\overline{N_\alpha}}{N} = \frac{1}{z+1}\xi_\alpha \frac{\partial \log \Xi_{z+1}}{\partial \xi_\alpha}, \tag{608, 24}$$

using formula (19) for $\Xi_{z+1}$. If we do this and make use of (20) and (23), we obtain after simplification just (21), and so obtain no new relations analogous to (23). Nor do we obtain anything new by considering groups of sites intermediate between a pair and the groups of $z+1$.

From (21) we deduce, using (20), that

$$\frac{\theta_\alpha}{\xi_\alpha \eta_\alpha^z} = \frac{\theta_\beta}{\xi_\beta \eta_\beta^z} = \dots = \frac{1}{\Sigma_\tau \xi_\tau \eta_\tau^z} = \frac{1}{\gamma \xi \eta^z}, \tag{608, 25}$$

and from (23) we deduce

$$\frac{\eta_\alpha}{\Sigma_\tau \xi_\tau \eta_\tau^{z-1}\eta_{\alpha\tau}} = \frac{\eta_\beta}{\Sigma_\tau \xi_\tau \eta_\tau^{z-1}\eta_{\beta\tau}} = . \tag{608, 26}$$

In (26) we have a set of simultaneous equations in number sufficient to determine the ratios $\eta_\alpha : \eta_\beta : \dots$ as functions of the known quantities $\xi_\alpha, \dots$ and $\eta_{\alpha\beta}, \dots$, and so by (25) to determine $\theta_\alpha, \theta_\beta, \dots$ as functions of $\xi_\alpha, \dots$ and $\eta_{\alpha\beta}, \dots$. Since, however, the equations (26) are of degree $z$ in $\eta_\alpha, \eta_\beta, \dots$, they are intractable, and this method of attack cannot generally lead to explicit formulae for $\theta_\alpha, \theta_\beta, \dots$. We can, however, obtain all the results that we require by an alternative procedure.

Just as we have obtained formulae for $\theta_\alpha$ by using (4), so by using (5) we can obtain formulae for $\theta_{\alpha\beta}$, the fraction of pairs of neighbouring sites occupied the one in the manner $\alpha$, the other in the manner $\beta$. It is simplest to combine (5) with (18) for $\Xi_2$, regarded as the $\Xi$ for a pair of sites in the field due to the remaining sites. We thus obtain

$$\theta_{\alpha\beta} = \frac{\overline{N_{\alpha\beta}}}{\frac{1}{2}zN} = \eta_{\alpha\beta}\frac{\partial \log \Xi_2}{\partial \eta_{\alpha\beta}} = \frac{2}{\sigma_{\alpha\beta}} \frac{\xi_\alpha \eta_\alpha^{z-1} \xi_\beta \eta_\beta^{z-1} \eta_{\alpha\beta}}{\gamma^2 \xi^2 \eta^{2z-1}}, \tag{608, 27}$$

where $\sigma_{\alpha\beta}$ is a symmetry number equal to 2 when $\alpha$ and $\beta$ are identical and 1 otherwise. From (27) we can deduce a number of relations such as

$$\frac{\theta_{\alpha\beta}\theta_{\gamma\delta}}{\theta_{\alpha\gamma}\theta_{\beta\delta}} = \frac{\eta_{\alpha\beta}\eta_{\gamma\delta}}{\eta_{\alpha\gamma}\eta_{\beta\delta}} \bigg/ \frac{\sigma_{\alpha\beta}\sigma_{\gamma\delta}}{\sigma_{\alpha\gamma}\sigma_{\beta\delta}}, \tag{608, 28}$$

and in particular

$$\frac{\theta_{\alpha\beta}^2}{\theta_{\alpha\alpha}\theta_{\beta\beta}} = \frac{4\eta_{\alpha\beta}^2}{\eta_{\alpha\alpha}\eta_{\beta\beta}} = 4e^{-(2w_{\alpha\beta}-w_{\alpha\alpha}-w_{\beta\beta})/kT}. \tag{608, 29}$$

It is remarkable[A] that these relations, from which the quantities $\eta_\alpha, \eta_\beta, \ldots$ as well as $\xi$, $\eta$, $\gamma$ have been completely eliminated, have been obtained from (18) without any use being made of (23). It will be noticed that these relations have the simple form of a quasi-chemical equilibrium. In § 610 we shall describe how these equations can be used to determine the thermodynamic functions of a regular assembly.

**§ 609. Nature of approximation.** The formulae, which have been derived for regular assemblies, are accurate only in so far as the average state of any selected site is completely determined by the states of its immediate neighbours. But strictly the probability for a selected site to be occupied in a particular way can never be completely independent of the manner of occupation of every other site however distant from the selected site. For suppose a certain site is specified as occupied in a certain way, then the probabilities of occupation in various ways of its immediate neighbours are immediately affected; but this affects the probabilities of the next neighbours and these in turn those of their neighbours and so on. Thus strictly the probabilities of occupation of each site are linked at least remotely to those of every other site however distant.

The analytical form of the approximation consists in using the same factors $\eta_\alpha, \eta_\beta, \ldots$ in whatever manner the other sites, other than immediate neighbours, are occupied. We have seen that subject to this approximation we can use the same value for these factors whether we consider a single site, a pair of sites or a group of a central site with its $z$ neighbours. We should continue to obtain mutually consistent equations for even larger groups of sites provided these contain only branches but no rings (in the terminology of organic chemistry). But as soon as we consider a group containing a closed ring we obtain different results.

For simplicity let us consider a square array with two manners of occupation $\alpha$ and $\beta$. Then we have for a single site

$$\Xi_1 = (\xi_\alpha \eta_\alpha^4 + \xi_\beta \eta_\beta^4)\,\gamma^{N-1}\xi^{N-1}\eta^{2N-4}. \qquad (609, 1)$$

For a pair of sites we have

$$\Xi_2 = \{\xi_\alpha \eta_\alpha^3(\xi_\alpha \eta_\alpha^3 \eta_{\alpha\alpha} + \xi_\beta \eta_\beta^3 \eta_{\alpha\beta}) + \xi_\beta \eta_\beta^3(\xi_\alpha \eta_\alpha^3 \eta_{\alpha\beta} + \xi_\beta \eta_\beta^3 \eta_{\beta\beta})\}\,\gamma^{N-2}\xi^{N-2}\eta^{2N-7}. \qquad (609, 2)$$

For a central site with its four neighbours we have

$$\Xi_5 = \{\xi_\alpha(\xi_\alpha \eta_\alpha^3 \eta_{\alpha\alpha} + \xi_\beta \eta_\beta^3 \eta_{\alpha\beta})^4 + \xi_\beta(\xi_\alpha \eta_\alpha^3 \eta_{\alpha\beta} + \xi_\beta \eta_\beta^3 \eta_{\beta\beta})^4\}\,\gamma^{N-5}\xi^{N-5}\eta^{2N-16}. \qquad (609, 3)$$

As we have seen, these forms for $\Xi$ are all mutually consistent with the same values for $\eta_\alpha$, $\eta_\beta$. If, however, we construct $\Xi_4$ for a group of four sites

[A] Compare however, § A10 in the appendix.

forming a square, we find

$$\Xi_4 = \{(\xi_\alpha \eta_\alpha^2)^4 \eta_{\alpha\alpha}^4 + 4(\xi_\alpha \eta_\alpha^2)^3 \xi_\beta \eta_\beta^2 \eta_{\alpha\alpha}^2 \eta_{\alpha\beta}^2 + (\xi_\alpha \eta_\alpha^2)^2 (\xi_\beta \eta_\beta^2)^2 (4\eta_{\alpha\alpha} \eta_{\alpha\beta}^2 \eta_{\beta\beta} + 2\eta_{\alpha\beta}^4)$$
$$+ 4\xi_\alpha \eta_\alpha^2 (\xi_\beta \eta_\beta^2)^3 \eta_{\alpha\beta}^2 \eta_{\beta\beta}^2 + (\xi_\beta \eta_\beta^2)^4 \eta_{\beta\beta}^4\} \gamma^{N-4} \xi^{N-4} \eta^{2N-12}, \quad (609, 4)$$

a $\Xi_4$ which is not equal to $\Xi_1$, $\Xi_2$, $\Xi_5$, with the same values of $\eta_\alpha$, $\eta_\beta$. This inconsistency exposes the nature of the approximation.

It is almost obvious that the more closely the sites are packed, the smaller will be the least group which manifests the inconsistency and the more serious the approximation of our treatment. For a closest packed lattice our constructions of $\Xi_1$ and $\Xi_2$ are consistent with each other but not with that for $\Xi_{z+1}$. This inaccuracy has been investigated by Rushbrooke* for the particular case of regular solutions, and shown not to be serious even for a closest packed lattice.

§ 610. **Thermodynamic functions of regular assemblies.** We have already mentioned that equations (608, 26) are just sufficient in number to determine the unknown quantities $\eta_\alpha, \eta_\beta, \ldots$ in terms of the known quantities $\xi_\alpha, \xi_\beta, \ldots$ and $\eta_{\alpha\beta}, \ldots$, and so to evaluate the grand partition function. Since, however, the equations (608, 26) are of degree $z$ in $\eta_\alpha, \eta_\beta, \ldots$ they are intractable, and this method of attack cannot generally lead to explicit formulae for the thermodynamic functions. We therefore use a quite different procedure depending on the use of equations (608, 29). Although the number of independent equations of the form (608, 29) is greater than the number of the form (608, 26), the former are considerably more tractable because they are quadratic in the unknowns $\theta_{\alpha\alpha}, \theta_{\alpha\beta}, \theta_{\beta\beta}, \ldots$, whereas the latter are of degree $z$ in the unknowns $\eta_\alpha, \eta_\beta, \ldots$.

We use these equations of quasi-chemical equilibrium (608, 29) in combination with the necessary equalities (608, 2) to determine $\overline{N_{\alpha\beta}}, \ldots$ in terms of $\overline{N_\alpha}, \overline{N_\beta}, \ldots$ and the known quantities $w_{\alpha\alpha}, w_{\alpha\beta}, w_{\beta\beta}, \ldots$. We shall show that the knowledge thus obtained of $\overline{N_{\alpha\beta}}, \ldots$ is sufficient to enable us to evaluate ordinary partition function of the assembly, and so to construct the free energy and the energy. In adopting this procedure we use the grand partition function only for the purpose of deriving the equations of quasi-chemical equilibrium (608, 29). Having obtained these we abandon the grand partition function and use these equations to evaluate the ordinary partition function.

The ordinary partition function corresponding to (608, 3) for an assembly with given $N_\alpha, N_\beta, \ldots$, instead of given $\lambda_\alpha, \lambda_\beta, \ldots$ as previously, is

$$\phi_\alpha^{N_\alpha} \phi_\beta^{N_\beta} \ldots \sum_{N_{\alpha\beta}, \ldots} g(N_{\alpha\beta}, \ldots) e^{-\Sigma N_{\alpha\beta} w_{\alpha\beta}/kT}, \quad (610, 1)$$

* Rushbrooke, *Proc. Roy. Soc.* A, **166**, 296 (1938).

where $g(N_{\alpha\beta}, \ldots)$ denotes the number of distinguishable configurations with the specified values of $N_{\alpha\beta}, \ldots$ which are subject to the necessary relations (608, 2). We now define quantities $\overline{\overline{N_{\alpha\beta}}}, \ldots$ such that

$$e^{-\Sigma \overline{\overline{N_{\alpha\beta}}} w_{\alpha\beta}/kT} \sum_{N_{\alpha\beta}, \ldots} g(N_{\alpha\beta}, \ldots) = \sum_{N_{\alpha\beta}, \ldots} g(N_{\alpha\beta}, \ldots) e^{-\Sigma N_{\alpha\beta} w_{\alpha\beta}/kT}, \quad (610, 2)$$

while the true average values $\overline{N_{\alpha\beta}}, \ldots$ are given by

$$\overline{N_{\alpha\beta}} \sum_{N_{\alpha\beta}, \ldots} g(N_{\alpha\beta}, \ldots) e^{-\Sigma N_{\alpha\beta} w_{\alpha\beta}/kT} = \sum_{N_{\alpha\beta}, \ldots} N_{\alpha\beta}\, g(N_{\alpha\beta}, \ldots) e^{-\Sigma N_{\alpha\beta} w_{\alpha\beta}/kT}. \quad (610, 3)$$

By taking logarithms of (2) and differentiating with respect to $T$ we can verify that

$$\overline{N_{\alpha\beta}} = -T^2 \frac{\partial(\overline{\overline{N_{\alpha\beta}}}/T)}{\partial T}. \quad (610, 4)$$

The free energy $F$ of the assembly according to (1) is given by

$$F = -\Sigma_\alpha N_\alpha kT \log \phi_\alpha - kT \log \sum_{N_{\alpha\beta}, \ldots} g(N_{\alpha\beta}, \ldots) e^{-\Sigma N_{\alpha\beta} w_{\alpha\beta}/kT}. \quad (610, 5)$$

Using (2) we can rewrite this as

$$\begin{aligned} F &= -\Sigma_\alpha N_\alpha kT \log \phi_\alpha - kT \log \sum_{N_{\alpha\beta}, \ldots} g(N_{\alpha\beta}, \ldots) + \Sigma_{\alpha\beta} \overline{\overline{N_{\alpha\beta}}} w_{\alpha\beta} \\ &= -\Sigma_\alpha N_\alpha kT \log \phi_\alpha - kT \log(N!/N_\alpha!\, N_\beta! \ldots) + \Sigma_{\alpha\beta} \overline{\overline{N_{\alpha\beta}}} w_{\alpha\beta} \\ &= \Sigma_\alpha N_\alpha kT \log \frac{N_\alpha}{N\phi_\alpha} + \Sigma_{\alpha\beta} \overline{\overline{N_{\alpha\beta}}} w_{\alpha\beta}. \end{aligned} \quad (610, 6)$$

We see that the contribution of the interaction energies to the free energy of the assembly is

$$F^{\text{int}} = \Sigma_{\alpha\beta} \overline{\overline{N_{\alpha\beta}}} w_{\alpha\beta}. \quad (610, 7)$$

The corresponding contribution to the total energy $E$ is

$$E^{\text{int}} = -T^2 \frac{\partial(F^{\text{int}}/T)}{\partial T} = \Sigma_{\alpha\beta} \overline{N_{\alpha\beta}} w_{\alpha\beta} \quad (610, 8)$$

according to (4).

We now rewrite equations (608, 29) in the form

$$\frac{\overline{N_{\alpha\beta}}}{\overline{N_{\alpha\alpha}}\, \overline{N_{\beta\beta}}} = 4e^{(2w_{\alpha\beta} - w_{\alpha\alpha} - w_{\beta\beta})/kT}, \quad (610, 9)$$

and we notice that there are just as many such equations as quantities $\overline{N_{\alpha\beta}}$ $(\alpha \neq \beta)$. According to (608, 2) we have

$$2N_{\alpha\alpha} + \sum_{\alpha \neq \beta} N_{\alpha\beta} = zN_\alpha, \quad (610, 10)$$

and we notice that there are just as many such equations as quantities $N_{\alpha\alpha}$. Thus equations (9) and (10) together are just sufficient in number to deter-

mine the quantities $\overline{N_{\alpha\alpha}}, \overline{N_{\beta\beta}}, \ldots$ and $\overline{N_{\alpha\beta}}, \ldots$ in terms of $N_\alpha, N_\beta, \ldots$. We thus obtain just the information required to make formulae (7) and (8) useful.

This outline of the treatment of regular assemblies is admittedly brief, but will be amplified in its application to regular solutions in Chapter VIII, and to regular monolayers in Chapter X.

**§ 611. Further generalization of partition functions.** We recall that in Chapter I one of our fundamental premises was that, for an assembly of given $E$, $V$, $N$, we obtain all equilibrium properties by averaging over all accessible states (complexions) of the assembly, attaching a weight 1 to each such state (degenerate states being counted with their correct multiplicity). We then showed in Chapter II that, for an assembly of given $T$, $V$, $N$, we can obtain all equilibrium properties by averaging over all accessible states of the assembly, attaching a weight $e^{-E/kT}$ to each such state. In the present chapter we have further shown that, for an assembly of given $T$, $V$, $\mu$, we can obtain all equilibrium properties by averaging over all accessible states of the assembly, attaching a weight $e^{-(E-N\mu)/kT}$ to each state.* It is equally possible† to deduce formulae for the average properties of an assembly of given $T$, $P$, $N$ or of given $T$, $P$, $\mu$. We have merely to average over all accessible states of the assembly, attaching to each such state a weight $e^{-(E+PV)/kT}$ for given $T$, $P$, $N$, or $e^{-(E+PV-N\mu)/kT}$ for given $T$, $P$, $\mu$. We shall not give any proofs, as these would be exactly parallel to those for the sets of independent variables already used. One method of proof would be to express the number of accessible states, subject to the prescribed values of the independent variables, as contour integrals and apply the method of steepest descents. Alternatively the correctness of the rules just laid down can be verified from the fact that they lead to consequences thermodynamically equivalent to those for the previous sets of independent variables.

We see then that for each set of independent variables we have a different weighting factor, which we denote by§ $w$, for each accessible state of the assembly consistent with the prescribed values of the independent variables. If we form the sum $\Sigma w$ over all accessible states, we obtain in each case a different function, and we propose to call each such function the *generalized partition function* for the particular set of variables. The ordinary partition function $f(T)$ is then the generalized partition function for the independent variables $T$, $V$, $N$, while the grand partition function $\Xi$ is the generalized partition function for the independent variables $T$, $V$, $\mu$. It can further be verified that for each set of independent variables the function $k \log \Sigma w$ is equal to a thermodynamic potential for the chosen variables.

* For brevity we write $N$ and $N\mu$ instead of $N_A, N_B, \ldots$ and $\Sigma_A N_A \mu_A$.

† Guggenheim, *J. Chem. Phys.* 7, 103 (1939).

§ This $w$ will not be confused with the interaction energies $w_{\alpha\alpha}, w_{\alpha\beta}, \ldots$.

All these statements and relationships are summarized in Table 1. The remaining sets of independent variables $E$, $V$, $\mu$ or $E$, $P$, $N$ or $E$, $P$, $\mu$ are of little physical interest, owing to the difficulty of prescribing a fixed value for the energy of an assembly that is not completely closed.

TABLE 1

| Independent variables | Weighting factor $w$ for each accessible state of assembly | Usual name for $\Sigma w$ | Thermodynamic potential equal to $k \log \Sigma w$ |
|---|---|---|---|
| $E, V, N$ | 1 | Weight | $S$ |
| $T, V, N$ | $e^{-E/kT}$ | Partition function | $-F/T$ |
| $T, V, \mu$ | $e^{-(E-N\mu)/kT}$ | Grand partition function | $PV/T$ |
| $T, P, N$ | $e^{-(E+PV)/kT}$ | | $-G/T$ |
| $T, P, \mu$ | $e^{-(E+PV-N\mu)/kT}$ | | 0 |

We shall not explicitly use any of the new generalized partition functions, although many of the discussions of condensed phases (solids and liquids) can in fact be made simpler by choosing $P$ instead of $V$ as an independent variable, and using the appropriate generalized partition function.

# CHAPTER VII

## IMPERFECT GASES

**§ 700. General gaseous assemblies with molecules not fully independent.** We now take up the discussion of imperfect gases. These assemblies differ essentially from perfect gases only because there is in the energy of the assembly as a whole a general term which is a function of the positional coordinates of all the constituent systems. Let us suppose that two systems (molecules) $\alpha$ and $\beta$ have energies $\epsilon_\alpha$, $\epsilon_\beta$ when they are very far apart. These energies will then be functions only of the coordinates or quantum numbers of the systems $\alpha$ and $\beta$ respectively, and each will be independent of the coordinates of the other. When, however, they approach each other, this independence must sooner or later cease. The energy of the pair will no longer be $\epsilon_\alpha+\epsilon_\beta$ but $\epsilon_\alpha+\epsilon_\beta+\epsilon_{\alpha\beta}$, say, where $\epsilon_{\alpha\beta}$ is a correcting term, at first small, depending on the coordinates, and strictly the velocities, of both systems. If, however, $\alpha$ and $\beta$ approach each other sufficiently slowly, then all the effects will be quasi-static,* and will depend only on relative coordinates, being independent of velocities. In this case, $\epsilon_{\alpha\beta}$ may legitimately be expected to behave like a potential energy depending only on the relative coordinates, whose derivatives give the forces. Moreover in actual applications nearly all molecular encounters are slow compared with the velocities of electrons in atoms and molecules, and will therefore be quasi-static. This is the assumption as to the nature of the interaction energy of $\epsilon_{\alpha\beta}$ tacitly made in all discussions of molecular interactions.

The function $\epsilon_{\alpha\beta}$ so specified must in general depend on the quantum states of the systems $\alpha$ and $\beta$. It is obvious that for atoms and molecules in general changes of electronic quantum numbers must affect $\epsilon_{\alpha\beta}$, but it is almost universal at ordinary temperatures for only one electronic state of the molecule to be relevant. It is often assumed, at least as an approximation, that $\epsilon_{\alpha\beta}$ is independent of molecular states of rotation and perhaps vibration. If it is not, then it is necessary to treat different rotational or vibrational states of molecules as different types of systems.

We shall use classical statistics throughout, since the errors so introduced are almost always negligible. We shall also assume that the translational

* By quasi-static we here mean what Ehrenfest [*Ann. d. Phys.* **51**, 327 (1916)] called "adiabatisch-reversibel". The latter expression is clumsy and has been contracted by subsequent writers to "adiabatic". This contraction is particularly objectionable, for the meaning intended is quite different from that accepted in thermodynamics and is much more closely related to the thermodynamic term "reversible". Other authors aware of this objection to "adiabatic" have guarded themselves by saying "adiabatic in Ehrenfest's sense", which is both clumsy and inaccurate, because Ehrenfest actually used "adiabatisch-reversibel" uncontracted.

kinetic and potential energy of the gas molecules may be handled classically. Here again the errors in question are usually small.*

**§ 701. Partition functions for the potential energy of the whole gas.** We can at once proceed to construct a partition function for the potential energy of the whole gas, which in conjunction with previous results will determine all the equilibrium properties.

Let us start by considering a *perfect* gas mixture, and examine how to construct a partition function for the whole classical energy of translation of its molecules. The internal energies of the molecules are independent of their translations, and will be accounted for as usual by separate partition functions. Let there be† $N_A, N_B, \ldots$ molecules of types $A, B, \ldots$, internal partition functions $j_A(T), j_B(T), \ldots$ and masses $m_A, m_B, \ldots$, supposed for the moment not to interact chemically. If $x_A, y_A, z_A, u_A, v_A, w_A$ are the position and velocity components of a system of type $A$, then a standard element of phase space for the whole gas has the extension

$$(m_A^{N_A} m_B^{N_B} \ldots)^3 \prod_{r=1}^{N_A} (dx_A \ldots dw_A)_r \prod_{s=1}^{N_B} (dx_B \ldots dw_B)_s \ldots, \qquad (701, 1)$$

and the weight

$$\frac{(m_A^{N_A} m_B^{N_B} \ldots)^3}{h^{3(N_A+N_B+\ldots)}} \prod_{r=1}^{N_A} (dx_A \ldots dw_A)_r \prod_{s=1}^{N_B} (dx_B \ldots dw_B)_s \ldots. \qquad (701, 2)$$

The classical partition function $L(T)$ for the translatory motion would therefore be given by

$$L(T) = \frac{(m_A^{N_A} m_B^{N_B} \ldots)^3}{h^{3(N_A+N_B+\ldots)}} \int \ldots \int e^{-\left[\sum_{r=1}^{N_A} \frac{1}{2} m_A(u_A^2+v_A^2+w_A^2)_r + \sum_{s=1}^{N_B} \frac{1}{2} m_B(u_B^2+v_B^2+w_B^2)_s + \ldots\right]/kT}$$
$$\times \prod^{N_A} (dx_A \ldots dw_A)_r \prod^{N_B} (dx_B \ldots dw_B)_s \ldots, \qquad (701, 3)$$

if we allowed ourselves to include permutations of like molecules. It is assumed here that there are no external fields of force except local boundary fields. All the space and velocity integrations in (3) are then independent, and can be carried out one by one. We must, however, remember that the integrations extend over all possible configurations, and in order not to count as distinct states several configurations differing only through the

* The necessary quantal generalization is largely due to Slater and Uhlenbeck and an excellent account of it has been given by Kahn, Dissertation *On the Theory of the Equation of State* (Utrecht, 1938).

† We shall use $A, B, \ldots$ to denote types of systems (molecules) and $N_A, N_B, \ldots$ for the numbers of systems of each type. $\Sigma_A$ denotes summation over all types and $\Sigma_{AB}$ summation over all pairs of types. On the other hand we shall use $\alpha, \beta$ to denote two selected systems which may or may not be of the same type. $\Sigma_\alpha$ then denotes summation over all systems, and is therefore equivalent to the operator $\Sigma_A N_A \times$. Similarly $\Sigma_{\alpha\beta}$ denotes summation over all pairs of systems and is equivalent to the operator $\Sigma_{AB} (N_A N_B/\sigma_{AB}) \times$, where $\sigma_{AB} = 1$ $(A \neq B)$ and $\sigma_{AA} = 2$.

interchange of two or more like molecules, we must divide (3) by $N_A!\,N_B!\,\ldots$. On performing the integrations, we then obtain

$$L(T) = \Pi_A \frac{1}{N_A!}\left\{\frac{(2\pi m_A kT)^{\frac{3}{2}} V}{h^3}\right\}^{N_A} = \Pi_A \frac{1}{N_A!}\{l_A(T)\}^{N_A}, \qquad (701,4)$$

where $l_A(T)$ denotes the ordinary partition function for the translations of a single molecule of the type $A$. For the complete partition function of the assembly we have to multiply $L(T)$ by the factor $\Pi_A\{j_A(T)\}^{N_A}$ for the internal degrees of freedom, and obtain

$$\Pi_A \frac{1}{N_A!}\{l_A(T)\,j_A(T)\}^{N_A} = \Pi_A \frac{1}{N_A!}\{f_A(T)\}^{N_A}. \qquad (701,5)$$

This partition function belongs to the whole assembly regarded as a single system, and is thus strictly analogous to the partition function $K(T)$ of a crystal. All the equilibrium properties of the gas can then be derived from $L(T)$ precisely in the same manner as those of a crystal are derived from $K(T)$. In particular for the free energy $F$ we have, using Stirling's theorem,

$$F = -kT\log\left[\Pi_A \frac{1}{N_A!}\{f_A(T)\}^{N_A}\right] = -\Sigma_A N_A kT\{\log f_A(T) - \log N_A + 1\}$$

$$= -\Sigma_A N_A kT\{\log l_A(T)\,j_A(T) - \log N_A + 1\}, \qquad (701,6)$$

in agreement with formula (225, 4), which was derived by treating each molecule as a separate system.

The extension to a classical imperfect gas is immediate. Under the specified conditions $j_A(T)$, $j_B(T)$, ... are still separable factors. The translational partition function $L(T)$ of the assembly is altered only by the addition to the energy of a term $W$ equal to the potential energy of the whole assembly, $W$ being thus a function of the positional coordinates of all the molecules. The inclusion of $W$ will not affect the velocity integrations. We therefore find for the complete partition function of the assembly, in place of (5),

$$\Pi_A\{\phi_A(T)\}^{N_A} \times \Omega(T), \qquad (701,7)$$

where

$$\phi_A(T) = \frac{(2\pi m_A kT)^{\frac{3}{2}}}{h^3}\,j_A(T), \qquad (701,8)$$

and

$$\Omega(T) = \frac{1}{N_A!\,N_B!\ldots}\int\ldots\int e^{-W/kT}\prod_{r=1}^{N_A}(dx_A\,dy_A\,dz_A)_r\prod_{s=1}^{N_B}(dx_B\,dy_B\,dz_B)_s\ldots. \qquad (701,9)$$

We note that $\phi_A(T)$ is the partition function for a molecule $A$ in a perfect gas with the factor $V$ omitted. $\Omega(T)$, which takes the place of $\Pi_A\,V^{N_A}/N_A!$ for a perfect gas, is conveniently referred to as the partition function for the configurational potential energy.

The integrals in $\Omega(T)$ are extended over the whole positional phase space available to the gas. If the gas is perfect, $W$ vanishes and $\Omega(T)$ reduces to $V^{N_A+N_B+\cdots}/N_A!\,N_B!\ldots$. It is assumed that in no case can $W \to -\infty$ but that ultimately there must be repulsive fields between any two particles so that $W$ tends to infinity, or at least to a large positive value, when they approach sufficiently closely. This assumption conforms to what we can deduce *a priori* from the quantum theory of the interaction of two molecular systems.

From the form of (7) it is clear that classical potential and kinetic energies in a gas can always be handled with separate partition functions. The kinetic energy can be dealt with in the ordinary way, as if the gas were perfect, by ordinary partition functions $\phi(T)$ without the $V$-factors. The potential energy is accounted for by $\Omega(T)$. It should be observed also that (7), (8) and (9) are perfectly general, so long as all the molecules are free to move individually, and apply to classical assemblies in which the imperfections are of any degree and the intermolecular forces of any range, and whether or no there are external fields of force. It is not necessarily true for higher degrees of imperfection and higher degrees of accuracy that $W$ can be regarded as built up entirely of terms such as $\epsilon_{\alpha\beta}$, that is, terms arising from binary interactions. This approximation is, however, adequate for most purposes and will be used throughout this chapter.

If there are no external fields of force, $W$ will be a function only of the relative coordinates of the molecules. If there are local boundary fields representing walls of the enclosure, this will still be true in the limit when the whole volume is large compared with the volume affected by the local fields.

By using (7) for the partition function of the whole gas, we now obtain for the free energy in place of (6)

$$F = -\Sigma_A N_A kT \log \phi_A(T) - kT \log \Omega(T). \qquad (701, 10)$$

If then we denote by $F^{\text{int}}$ the contribution of the intermolecular forces to $F$, we see by comparison of (10) and (6) that

$$F^{\text{int}} = -kT \log \Omega(T) + kT\, \Sigma_A N_A\{\log(V/N_A)+1\}. \qquad (701, 11)$$

The corresponding contribution $E^{\text{int}}$ to the total energy is

$$E^{\text{int}} = -T^2 \frac{\partial (F^{\text{int}}/T)}{\partial T} = kT^2 \frac{\partial \log \Omega(T)}{\partial T}. \qquad (701, 12)$$

It is convenient to introduce an abbreviated notation into $\Omega(T)$. We write $(d\omega_A)_r$ for $(dx_A\, dy_A\, dz_A)_r$ and contract $\prod_{r=1}^{N_A} (d\omega_A)_r \prod_{s=1}^{N_B} (d\omega_B)_s \ldots$ into $\Pi_A (d\omega_A)^{N_A}$. Thus

$$\Omega(T) = \frac{1}{N_A!\,N_B!\ldots} \int \cdots \int e^{-W/kT}\, \Pi_A (d\omega_A)^{N_A}. \qquad (701, 13)$$

If now $Q$ is any function of the configurational coordinates of the molecules, the average value $\bar{Q}$ of $Q$ is given by

$$\bar{Q} = \frac{\int \dots \int Q e^{-W/kT} \Pi_A (d\omega_A)^{N_A}}{\int \dots \int e^{-W/kT} \Pi_A (d\omega_A)^{N_A}}. \qquad (701, 14)$$

In particular the average value $\overline{W}$ of the intermolecular energy $W$ is

$$\overline{W} = \frac{\int \dots \int W e^{-W/kT} \Pi_A (d\omega_A)^{N_A}}{\int \dots \int e^{-W/kT} \Pi_A (d\omega_A)^{N_A}} = kT^2 \frac{\partial \log \Omega(T)}{\partial T}. \qquad (701, 15)$$

By comparison of (12) and (15) we see that

$$E^{\text{int}} = \overline{W}, \qquad (701, 16)$$

as is physically obvious.

If the configurational potential energy $W$ depends on some external parameter $x$, which does not affect the internal degrees of freedom, then the average value $\bar{X}$ of the generalized force corresponding to this parameter will be

$$\bar{X} = -\overline{\frac{\partial W}{\partial x}} = \frac{\int \dots \int \left(-\frac{\partial W}{\partial x}\right) e^{-W/kT} \Pi_A (d\omega_A)^{N_A}}{\int \dots \int e^{-W/kT} \Pi_A (d\omega_A)^{N_A}}$$

$$= kT \frac{\partial}{\partial x} \log \Omega(T). \qquad (701, 17)$$

By comparing (17) with (10) we can verify the thermodynamic relation

$$\bar{X} = -\left(\frac{\partial F}{\partial x}\right)_T. \qquad (701, 18)$$

The most important application of (17) is when $x$ is the volume $V$ and $\bar{X}$ the pressure $P$. We then have

$$P = kT \frac{\partial \log \Omega(T)}{\partial V}. \qquad (701, 19)$$

It is particularly obvious in this section that the partition functions of our theory are identical with the separable factors in the phase integrals of Gibbs.

§ **702. Molecular distribution laws.** The ordinary uniform space distribution law may be established for a gas of any degree of imperfection, when there are no external fields or long range forces, as follows. By long range forces we mean forces whose effects are sensible at distances of the

order of the dimensions of the assembly. To the accuracy of the quasi-classical approximation to $\Omega(T)$ with which we are working, the division by the factorials eliminates the reduplication of states due to permutations, but has no effect on the relative contributions of different parts of the integral factor. These relative contributions may be discussed purely classically without reference to symmetry requirements. That part of the integral factor which corresponds to the presence of a selected molecule $\alpha$ in a given volume element $\delta V$ is

$$\int_{(\delta V)} d\omega_\alpha \int_{(V)} \dots \int e^{-W/kT}\, \Pi'_A\, (d\omega_A)^{N_A}, \tag{702, 1}$$

just one $d\omega_\alpha$ integration over $V$ being omitted. If the corresponding contribution to $\Omega(T)$ is called $\delta\Omega(T)$, then the classical frequency ratio for the occurrence of the selected $\alpha$ in $\delta V$, or the fraction of a long time during which it will be found there, is given by

$$\frac{\delta\Omega(T)}{\Omega(T)} = \frac{\int_{(\delta V)} d\omega_\alpha \int_{(V)} \dots \int e^{-W/kT}\, \Pi'_A\, (d\omega_A)^{N_A}}{\int_{(V)} d\omega_\alpha \int_{(V)} \dots \int e^{-W/kT}\, \Pi'_A\, (d\omega_A)^{N_A}}. \tag{702, 2}$$

If there are no external fields, then $W$ depends only on the relative coordinates of the molecules, and if there are also no long range forces

$$\int_{(V)} \dots \int e^{-W/kT}\, \Pi'_A\, (d\omega_A)^{N_A}$$

must at a given temperature be a constant independent of the position of the selected $\alpha$ in $\delta V$ or of $\delta V$ in $V$. It then follows from (2) that

$$\delta\Omega(T)/\Omega(T) = \delta V/V. \tag{702, 3}$$

This applies to each of the molecules of the same type as $\alpha$, and therefore the average number of molecules of type $A$ to be found in $\delta V$ is simply $N_A \delta V/V$ as for a perfect gas.

A correct quantal treatment changes all the details of the argument, but the result is unaffected.

By a similar argument we see that the frequency ratio for the simultaneous occurrence of a selected pair of molecules $\alpha$, $\beta$ in selected $d\omega_\alpha$, $d\omega_\beta$ respectively must be given by

$$d\omega_\alpha\, d\omega_\beta \frac{\int_{(V)} \dots \int e^{-W/kT}\, \Pi''_A\, (d\omega_A)^{N_A}}{\int_{(V)} \dots \int e^{-W/kT}\, \Pi_A\, (d\omega_A)^{N_A}}, \tag{702, 4}$$

just two integrations over $V$ being omitted in the numerator.

When no effective long range* or external forces are present, the integral in the numerator of (3) must be a function only of the relative coordinates of the selected $d\omega_\alpha$ and $d\omega_\beta$. We may then write it in the form

$$Qe^{-W_{\alpha\beta}/kT},$$

where $W_{\alpha\beta}$ is defined so that $W_{\alpha\beta} \to 0$ at infinite separation, and $Q$ is constant. So defined, $W_{\alpha\beta}$ may depend on the average positions of a large number of other molecules and may therefore itself be a function of $T$. Again,

$$\iint Qe^{-W_{\alpha\beta}/kT}\, d\omega_\alpha d\omega_\beta = QV^2, \tag{702, 5}$$

provided only that $W_{\alpha\beta} \to 0$ rapidly for large separations, as in practice it always does. Thus the frequency ratio for the occurrence of the selected pair in the selected volume elements reduces to

$$e^{-W_{\alpha\beta}/kT}\, d\omega_\alpha d\omega_\beta / V^2. \tag{702, 6}$$

After integration with respect to $d\omega_\alpha$, we deduce that the average fraction of all molecules of the same type as $\beta$ in a selected $d\omega_\beta$ near a given molecule $\alpha$ anywhere in the assembly is

$$e^{-W_{\alpha\beta}/kT}\, d\omega_\beta / V. \tag{702, 7}$$

Formulae (6) and (7) are forms of Boltzmann's distribution law. It is important to realize, however, the precise meaning of $W_{\alpha\beta}$ for which the law is true. According to the definition of $W_{\alpha\beta}$ we have

$$Qe^{-W_{\alpha\beta}/kT} = \int_{(V)} \cdots \int e^{-W/kT}\, \Pi''_A\, (d\omega_A)^{N_A}. \tag{702, 8}$$

If we differentiate with respect to $x_\beta$ one of the coordinates of the $\beta$ in $d\omega_\beta$, since $Q$ is independent of $x_\beta$, we obtain

$$-\frac{1}{kT}\frac{\partial W_{\alpha\beta}}{\partial x_\beta}\int_{(V)} \cdots \int e^{-W/kT}\, \Pi''_A\, (d\omega_A)^{N_A} = \int_{(V)} \cdots \int -\frac{1}{kT}\frac{\partial W}{\partial x_\beta}\, e^{-W/kT}\, \Pi''_A\, (d\omega_A)^{N_A}, \tag{702, 9}$$

or

$$\frac{\partial W_{\alpha\beta}}{\partial x_\beta} = \overline{\frac{\partial W}{\partial x_\beta}} = {}^{\alpha\beta}\overline{X_\beta}, \tag{702, 10}$$

say, where ${}^{\alpha\beta}\overline{X_\beta}$ denotes the value of the force in the $x$-direction acting on the molecule $\beta$ at the given position relative to the molecule $\alpha$, *averaged over all positions of the remaining molecules*. Thus $W_{\alpha\beta}$ is the potential energy whose gradient gives the average force between the $\alpha$ and $\beta$ molecules. More loosely $W_{\alpha\beta}$ may be called the mutual free energy of the $\alpha$ and $\beta$ molecules in their given positions. In particular $W_{\alpha\beta}$ is not necessarily equal to $\epsilon_{\alpha\beta}$. Only in the case of short range forces with ternary and higher order interactions neglected shall we find that $W_{\alpha\beta} = \epsilon_{\alpha\beta}$ to the first approximation.

* We shall see in Chapter x that this allows of the consideration of electrostatic forces in ionic media of zero space charge.

**§ 703. A first approximation for imperfect gases. Short range forces.** To simplify the algebra we start by considering an assembly with only one type of molecule. The formulae obtained are easily extended to any number of types. We suppose that the region round $\alpha$ or $\beta$ in which $\epsilon_{\alpha\beta}$ is sensible is of strictly limited range, so that there is a small volume $v_{\alpha\beta}$ round $\alpha$ in which $\beta$ (or round $\beta$ in which $\alpha$) must lie so that $\epsilon_{\alpha\beta} \neq 0$. For the present we neglect external fields of force. We suppose that $W$ consists only of terms such as $\epsilon_{\alpha\beta}$, even when three or more molecules are in close interaction together. We shall also eventually suppose that $v_{\alpha\beta}$ is small compared with $V/N$ the available volume per molecule, and that terms of higher order than the first in $Nv_{\alpha\beta}/V$ may be neglected compared with unity. The terms that are to be neglected at any stage will require, however, the most careful scrutiny.

Whatever the size of $Nv_{\alpha\beta}/V$, we can write $\Omega(T)$ for a single molecular species in the form

$$\Omega(T) = \frac{1}{N!}\int_{(V)} \cdots \int \prod^{\frac{1}{2}N(N-1)\,\text{factors}} e^{-\epsilon_{\alpha\beta}/kT}\,(d\omega)^N, \qquad (703,1)$$

the number of factors in the product being equal to the number of ways of pairing $N$ molecules. In performing the integrations in $\Omega(T)$ we must include in the domain of integration configurations differing only by the interchange of two or more molecules, the error so introduced being eliminated by the divisor $N!$. We now define $\eta_{\alpha\beta}$ by the equation

$$\eta_{\alpha\beta} = e^{-\epsilon_{\alpha\beta}/kT} - 1, \qquad (703,2)$$

and rewrite (1) as

$$\Omega(T) = \frac{1}{N!}\int_{(V)} \cdots \int \prod^{\frac{1}{2}N(N-1)\,\text{factors}} (1+\eta_{\alpha\beta})\,(d\omega)^N. \qquad (703,3)$$

We now expand the integrand as a power series in the $\eta_{\alpha\beta}$, each different subscript $\alpha$, $\beta$, ... denoting a different molecule, and obtain

$$\Omega(T) = \frac{1}{N!}\int_{(V)} \cdots \int \{1 + \Sigma\,\eta_{\alpha\beta} + \Sigma\,\eta_{\alpha\beta}\eta_{\alpha\gamma} + \Sigma\,\eta_{\alpha\beta}\eta_{\beta\gamma}\eta_{\gamma\alpha} + \Sigma\,\eta_{\alpha\beta}\eta_{\gamma\delta} + \ldots\}\,(d\omega)^N. \qquad (703,4)$$

The term in $\Sigma\,\eta_{\alpha\beta}$ corresponds to configurations in which there is just one pair of molecules within range of each other's field of force. The term in $\Sigma\,\eta_{\alpha\beta}\eta_{\alpha\gamma}$ corresponds to configurations in which there are just two pairs of molecules interacting, these two pairs having one common molecule. The term in $\Sigma\,\eta_{\alpha\beta}\eta_{\beta\gamma}\eta_{\gamma\alpha}$ corresponds to configurations in which there are three molecules all interacting with one another, but no other molecules interacting. The term in $\Sigma\,\eta_{\alpha\beta}\eta_{\gamma\delta}$ corresponds to configurations in which there are two distinct pairs of molecules interacting. And so on.

We now make the important approximation of ignoring the simultaneous interaction of any molecule with more than one other molecule. This assumption* underlies all the formulae from here onwards until we come to § 722. It can be shown that when we make this approximation the evaluation of $\Omega(T)$ is correct only as far as terms of the first order in $Nv_{\alpha\beta}/V$. The approximation is therefore valid only when $Nv_{\alpha\beta}/V$ is small, that is to say for gases that are only slightly imperfect. Using this approximation we ignore terms such as that in $\eta_{\alpha\beta}\eta_{\alpha\gamma}$ (with a common $\alpha$) and (4) reduces to

$$\Omega(T) = \frac{1}{N!}\int_{(V)} \cdots \int \{1 + \Sigma\, \eta_{\alpha\beta} + \Sigma\, \eta_{\alpha\beta}\eta_{\gamma\delta} + \Sigma\, \eta_{\alpha\beta}\eta_{\gamma\delta}\eta_{\epsilon\zeta} + \ldots\}\, (d\omega)^N. \tag{703, 5}$$

We can now count the number of terms under each summation sign. The number of pairs $\alpha\beta$ is $\frac{1}{2}N!/(N-2)!$. The number of distinct sets of two pairs $\alpha\beta$ and $\gamma\delta$ is $(\frac{1}{2})^2 N!/\{(N-4)!\,2!\}$. The number of distinct sets of three pairs is $(\frac{1}{2})^3 N!/\{(N-6)!\,3!\}$. The number of distinct sets of $r$ pairs is $(\frac{1}{2})^r N!/\{(N-2r)!\,r!\}$. Using these enumerations in (5), we obtain

$$\Omega(T) = \frac{V^N}{N!} \sum_{r=0}^{\frac{1}{2}N} \frac{N!}{r!\,(N-2r)!\,N^r} \left\{\frac{1}{2}\frac{N}{V^2}\iint_{(V)} \eta_{\alpha\beta}\, d\omega_\alpha\, d\omega_\beta\right\}^r. \tag{703, 6}$$

But since $\eta_{\alpha\beta}$ depends only on the relative coordinates of the two molecules $\alpha$ and $\beta$, we can perform the integration over the coordinates of one of them. Thus

$$\iint_{(V)} \eta_{\alpha\beta}\, d\omega_\alpha\, d\omega_\beta = V\int \eta_{\alpha\beta}\, d\omega = V\int (e^{-\epsilon_{\alpha\beta}/kT} - 1)\, d\omega. \tag{703, 7}$$

In the last two integrals the range of integration is strictly $V$, but effectively only $v_{\alpha\beta}$. For brevity we introduce the quantity $\xi$ defined by

$$\xi = \frac{1}{2}\frac{N}{V^2}\iint_{(V)} \eta_{\alpha\beta}\, d\omega_\alpha\, d\omega_\beta = \frac{1}{2}\frac{N}{V}\int (e^{-\epsilon/kT} - 1)\, d\omega, \tag{703, 8}$$

there being no longer any need for the subscript $\alpha\beta$ in $\epsilon_{\alpha\beta}$. Substituting this into (6) we have

$$\Omega(T) = \frac{V^N}{N!} \sum_{r=0}^{\frac{1}{2}N} \frac{N!}{r!\,(N-2r)!\,N^r}\, \xi^r. \tag{703, 9}$$

* The statement, often made, that triple and higher order interactions are ignored is ambiguous. It can mean either (1) that the interaction energy $W$ is made up of a sum of terms like $\epsilon_{\alpha\beta}$, terms like $\epsilon_{\alpha\beta\gamma}$ being neglected, or (2) that all configurations are neglected in which terms such as $\epsilon_{\alpha\beta}$ and $\epsilon_{\alpha\gamma}$ (with a common $\alpha$) simultaneously differ appreciably from zero. We are here making both approximations, but their importance is vastly different. The former approximation is a good one even for highly compressed gases and liquids, and is retained in §§ 722 *sqq.* and in Chapter VIII. The latter approximation restricts us to gases that are only slightly imperfect. It must be removed if we want to deal with critical phenomena and liquids. It is because of this approximation that the application of van der Waals' equation to critical phenomena is fallacious.

It is obvious that the form of $\Omega(T)$, at least for the earlier terms, is approximately given by

$$\frac{V^N}{N!}\sum_{r=0}^{N}\frac{N!}{r!(N-r)!}\xi^r = \frac{V^N(1+\xi)^N}{N!}, \tag{703, 10}$$

and one is led to expect, as is in fact true, that

$$\Omega(T) = V^N\{1+\xi+O(\xi^2)\}^N/N!. \tag{703, 11}$$

The strict derivation of (11) is due to Ursell.* We shall omit the proof, as the analysis is far from simple. It is to be observed that it is *not* sufficient in order to derive (11) to retain only the first two terms in (9), as is commonly done, and assume that the second is small compared with the first and so on. For the ratio of the first two terms is $(N-1)\xi$ and it is only $\xi$ which we are entitled to assume small. Assuming then the truth of (11) we have, using Stirling's theorem and neglecting terms of higher order than the first in $Nv_{\alpha\beta}/V$,

$$\begin{aligned}\log\Omega(T) &= N\log\{V(1+\xi)\} - N\log N + N\\ &= N\left\{\log\frac{V}{N}+1\right\} + N\log\left\{1+\frac{1}{2}\frac{N}{V}\int(e^{-\epsilon/kT}-1)\,d\omega\right\}\\ &= N\left\{\log\frac{V}{N}+1\right\} + \frac{1}{2}\frac{N^2}{V}\int(e^{-\epsilon/kT}-1)\,d\omega.\end{aligned} \tag{703, 12}$$

For the general mixture an analogous treatment leads to

$$\begin{aligned}\log\Omega(T) &= \Sigma_A N_A\left\{\log\frac{V}{N_A}+1\right\} + \Sigma_A N_A\log\left\{1+\tfrac{1}{2}\Sigma_B\frac{N_B}{V}\int(e^{-\epsilon_{AB}/kT}-1)\,d\omega\right\}\\ &= \Sigma_A N_A\left\{\log\frac{V}{N_A}+1\right\} + \Sigma_{AB}\frac{N_A N_B}{\sigma_{AB}V}\int(e^{-\epsilon_{AB}/kT}-1)\,d\omega,\end{aligned} \tag{703, 13}$$

where $\sigma_{AB}$ is the usual symmetry number. In every case the terms omitted are of order smaller by the factor $\Sigma_B N_B v_{AB}/V$ than those retained.

The integral in (8) is more commonly expressed in polar coordinates, for by ignoring coordinates defining the orientation of molecules we have tacitly assumed that each $\epsilon$ is a function of $r$ alone, or may be replaced by a mean value for all orientations. Expressed thus (13) becomes

$$\log\Omega(T) = \Sigma_A N_A\left\{\log\frac{V}{N_A}+1\right\} + \Sigma_{AB}\frac{N_A N_B}{\sigma_{AB}V}\int(e^{-\epsilon_{AB}/kT}-1)\,4\pi r^2\,dr. \tag{703, 14}$$

The method can be extended to systems for which orientations are relevant, and the potential energy is a general function of relative position, but we shall not take up such extensions here.

* Ursell, *Proc. Camb. Phil. Soc.* **23**, 685 (1927). Many current analyses of this type are fallacious, e.g. Jeans, *Dynamical Theory of Gases*. Ed. 2, §218 (Cambridge, 1916); Fowler, *Proc. Camb. Phil. Soc.* **22**, 861 (1925).

We have hitherto assumed that $\epsilon_{AB}$ is due to forces of finite range. It is more usual and convenient in practice to represent molecular interactions by an energy which falls off like some inverse $m$th power of the distance. If $m > 3$, the integral in (8) or (14) will converge when extended over all space. Any such integral, if sufficiently rapidly convergent, can be substituted for the finite integral in (8) and elsewhere, without modification of the argument, for the integral over all space differs negligibly from the integral over a $v_{AB}$ of atomic dimensions. We thus find

$$\log \Omega(T) = \Sigma_A N_A \left\{\log \frac{V}{N_A} + 1\right\} + \Sigma_{AB} \frac{N_A N_B}{\sigma_{AB} V} \int_0^\infty (e^{-\epsilon_{AB}/kT} - 1)\, 4\pi r^2 dr. \tag{703, 15}$$

**§ 704. Thermodynamic properties of imperfect gases.** Having now obtained an approximate formula for $\Omega(T)$ valid for slightly imperfect gases, we can obtain all the thermodynamic functions by substituting the value of $\Omega(T)$ into the formulae of § 701. It is convenient to introduce the function $B_{AB}(T)$ defined by

$$B_{AB}(T) = \tfrac{1}{2} \int_0^\infty (1 - e^{-\epsilon_{AB}/kT})\, 4\pi r^2 dr. \tag{704, 1}$$

Using this in (703, 15), we have

$$\log \Omega(T) = \Sigma_A N_A \left\{\log \frac{V}{N_A} + 1\right\} - \Sigma_{AB} \frac{N_A N_B}{V} \frac{2B_{AB}(T)}{\sigma_{AB}}. \tag{704, 2}$$

Substituting (2) into (701, 10), we obtain for the free energy

$$\frac{F}{kT} = \Sigma_A N_A \left\{\log \frac{N_A}{\phi_A V} - 1\right\} + \Sigma_{AB} \frac{N_A N_B}{V} \frac{2B_{AB}(T)}{\sigma_{AB}}. \tag{704, 3}$$

From (3) we can derive all the other equilibrium properties by the usual thermodynamic formulae. Thus for the pressure we deduce

$$P = -\frac{\partial F}{\partial V} = kT \frac{\Sigma_A N_A}{V} + kT \Sigma_{AB} \frac{N_A}{V} \frac{N_B}{V} \frac{2B_{AB}(T)}{\sigma_{AB}}. \tag{704, 4}$$

For the partial potential $\mu_A$ per molecule $A$ we have

$$\mu_A = \left(\frac{\partial F}{\partial N_A}\right)_{T,V} = kT \log \frac{N_A}{\phi_A V} + kT \Sigma_B \frac{N_B}{V} 2B_{AB}(T). \tag{704, 5}$$

For the absolute activity $\lambda_A$ of the molecules $A$ we have

$$\lambda_A = e^{\mu_A/kT} = \frac{N_A}{\phi_A V}\left\{1 + \Sigma_B \frac{N_B}{V} 2B_{AB}(T)\right\}, \tag{704, 6}$$

to the degree of approximation to which our formulae are valid.

The fugacity $p_A^*$ of the species $A$ may be defined by

$$kT \log \frac{p_A^*(V)}{p_A(V_\infty)} = \mu_A(V) - \mu_A(V_\infty), \qquad (704, 7)$$

where $V_\infty$ is a volume so great that the gas becomes effectively ideal, and the fugacity $p_A^*(V_\infty)$ becomes effectively equal to the partial pressure $p_A(V_\infty)$. At the actual volume $V$ the fugacity is then given by

$$p_A^* = \frac{N_A kT}{V}\left\{1 + \Sigma_B \frac{N_B}{V} 2B_{AB}(T)\right\}. \qquad (704, 8)$$

For a simple gas of molecules $A$, if we introduce the molecular volume $v$ defined by

$$v = V/N_A, \qquad (704, 9)$$

the above formulae reduce to

$$Pv = kT\left\{1 + \frac{B(T)}{v}\right\}, \qquad (704, 10)$$

$$\mu = -kT \log \phi v + kT \frac{2B(T)}{v}, \qquad (704, 11)$$

$$p^* = \frac{kT}{v}\left\{1 + \frac{2B(T)}{v}\right\}. \qquad (704, 12)$$

If we denote by $P^{\mathrm{id}}$ the quantity $kT/v$, which is equal to the pressure for a perfect gas, then we see by comparison of (10) and (12) that

$$p^* - P = P - P^{\mathrm{id}}, \qquad (704, 13)$$

or correct to the same order

$$\frac{p^*}{P} = \frac{P}{P^{\mathrm{id}}}. \qquad (704, 14)$$

Formula (14) is due to Lewis† and has been used by his school to compute the fugacity $p^*$ corresponding to a given pressure $P$. There is, however, no simple relation similar to (14) applicable to mixtures of imperfect gases.

Another important thermodynamic quantity in an imperfect gas is the Joule-Thomson coefficient, which determines the temperature change for a given pressure drop when a gas is forced through a porous plug. Its value is given by‡

$$\left(\frac{\partial T}{\partial P}\right)_{E+PV} = \frac{-V + T\left(\frac{\partial V}{\partial T}\right)_P}{C_P}. \qquad (704, 15)$$

We shall consider only the limiting form of (15) at low pressures. We therefore use the formula for $V$

$$Pv = kT + PB(T), \qquad (704, 16)$$

† Lewis and Randall, *Thermodynamics*, p. 198 (McGraw-Hill, 1923).

‡ See *M.T.* p. 48.

which is equivalent to (10) correct to the terms of the first order in $B(T)/V$. From (16) we deduce for low pressures

$$T\left(\frac{\partial V}{\partial T}\right)_P = \frac{kT}{P} + T\frac{dB(T)}{dT}. \qquad (704, 17)$$

Substituting (17) into (15), we find for the Joule-Thomson coefficient in the limit of low pressures

$$\left(\frac{\partial T}{\partial P}\right)_{E+PV} = \frac{-B(T) + T\dfrac{dB(T)}{dT}}{C_P} = \frac{T^2}{C_P}\frac{d\left(\dfrac{B}{T}\right)}{dT}. \qquad (704, 18)$$

It is to be noticed that as $P$ tends to zero, the Joule-Thomson coefficient tends to a definite limit, which may be positive or negative. The Joule-Thomson coefficient, in the limit of low pressures, can vanish only at a single temperature determined by the condition

$$\frac{d(B/T)}{dT} = 0. \qquad (704, 19)$$

The temperature at which (19) is satisfied is called the *Joule-Thomson inversion temperature* (for the limit of low pressures).

**§ 705. Alternative treatment as a problem of association.** The results of §§ 703, 704 can be reached in a variety of other ways, one of which will now be considered. We shall confine ourselves to the case of an imperfect gas of $N$ similar molecules.

The results for a perfect gas can be extended at once to an imperfect gas (short range forces) by the device of regarding any pair of molecules within each other's field of force as a *system* to be discussed as a whole. Any single molecule outside the fields of force remains a system as before. The equilibrium state of the assembly can then be studied explicitly as a problem in association of perfect gases. We consider only interactions in pairs. Let $N$ denote the total number of molecules, $N_1$ the number of free molecules and $N_2$ the number of molecular pairs, so that

$$N_1 + 2N_2 = N. \qquad (705, 1)$$

Then the equilibrium between molecular pairs and free molecules is given by

$$\frac{N_2}{N_1^2} = \frac{f_2(T)}{\{f_1(T)\}^2}, \qquad (705, 2)$$

where $f_1(T)$ is the partition function of a free molecule, and $f_2(T)$ that of a molecular pair. Now whereas $f_1(T)$ contains as a factor $j(T)$, the partition function for the internal degrees of freedom, $f_2(T)$ contains the factor

$\{j(T)\}^2$. Hence the internal partition functions cancel and (2) reduces to

$$\frac{N_2}{N_1^2} = \frac{l_2(T)}{\{l_1(T)\}^2}, \tag{705, 3}$$

where $\{l_1(T)\}^2$, $l_2(T)$ are the partition functions for the translational degrees of freedom of the two molecules, when free and when forming a molecular pair respectively. Now these degrees of freedom are effectively classical, so that the kinetic and potential energies separate. Each of the partition functions $l_1(T)$, $l_2(T)$ is therefore the product of a factor for the kinetic energy and another for the potential energy. The kinetic factors clearly cancel and (3) reduces further to

$$\frac{N_2}{N_1^2} = \frac{u_2(T)}{\{u_1(T)\}^2}, \tag{705, 4}$$

where $u_1(T)$, $u_2(T)$ are the partition functions for the potential energy of the molecules, when free and when forming a molecular pair respectively. We denote the coordinates of the two molecules by the subscripts $\alpha$, $\beta$ respectively, but we can without ambiguity write $\epsilon$ instead of $\epsilon_{\alpha\beta}$ for their mutual potential energy. Then

$$u_1(T) = \int d\omega_\alpha = \int d\omega_\beta, \tag{705, 5}$$

$$u_2(T) = \tfrac{1}{2}\iint e^{-\epsilon/kT}\, d\omega_\alpha\, d\omega_\beta, \tag{705, 6}$$

the factor $\frac{1}{2}$ in $u_2(T)$ being due to the symmetry number 2. The range of integration of $u_1(T)$ is not the whole volume $V$, because if any one molecule is in the field of another the two rank as a molecular pair, and not as free molecules. It appears at first that the range of integration for $u_1(T)$ is $V - Nv_0$, where $v_0$ is the volume around a single molecule in which its field is appreciable. This, however, would not be correct, as it would lead to counting the whole of each excluded volume twice over, once for each member of the pair. To avoid doing this we should integrate over the volume $V$ for one of the two factors $u_1(T)$ in (4) and over the volume $V - Nv_0$ for the other factor. We obtain the same final result in a more symmetrical manner to the required accuracy by integrating over $V - \frac{1}{2}Nv_0$ for each factor. Adopting this convention, we have

$$u_1(T) = \int_{V-\frac{1}{2}Nv_0} d\omega = V - \tfrac{1}{2}Nv_0. \tag{705, 7}$$

The range of integration for $d\omega_\alpha$, $d\omega_\beta$ in (6) is that for which $\epsilon$ is appreciable. Now $\epsilon$ depends only on the relative positions of the two molecules. We may therefore write (6) as

$$u_2(T) = \tfrac{1}{2}V \iiint e^{-\epsilon(\xi,\eta,\zeta)/kT}\, d\xi\, d\eta\, d\zeta, \tag{705, 8}$$

where $\xi$, $\eta$, $\zeta$ are the cartesian coordinates of one molecule relative to the other. Changing to relative polar coordinates, we find

$$u_2(T) = \tfrac{1}{2}V\int_0^{r_0} e^{-\epsilon(r)}\,4\pi r^2\,dr, \tag{705, 9}$$

where $r_0$ is the effective range of the intermolecular forces defined by

$$v_0 = \tfrac{4}{3}\pi r_0^3. \tag{705, 10}$$

It is convenient to define $A(T)$ by

$$A(T) = \tfrac{1}{2}\int_0^{r_0} e^{-\epsilon(r)/kT}\,4\pi r^2\,dr$$
$$= \tfrac{2}{3}\pi r_0^3 - B(T). \tag{705, 11}$$

According to (4), (7) and (9) we have then

$$\frac{N_2}{N_1^2} = \frac{VA(T)}{(V-\tfrac{1}{2}Nv_0)^2}. \tag{705, 12}$$

Therefore correct to terms of order $(Nv_0/V)$ we have

$$N_2 = N_1^2A(T)/V = N^2A(T)/V, \tag{705, 13}$$

$$N_1 = N - 2N_2 = N - 2N^2A(T)/V. \tag{705, 14}$$

We can now derive the free energy for the assembly. In place of the terms

$$NkT\{\log(N/V)-1\} \tag{705, 15}$$

for a perfect gas, we have the terms

$$N_1kT\left\{\log\frac{N_1}{u_1(T)}-1\right\}+N_2kT\left\{\log\frac{N_2}{u_2(T)}-1\right\}. \tag{705, 16}$$

The contribution $F^{\text{int}}$ due to the intermolecular forces is the difference between (16) and (15). Thus, using (1) we obtain

$$F^{\text{int}} = N_1kT\log\frac{N_1}{u_1(T)}+N_2kT\log\frac{N_2}{u_2(T)}-NkT\log\frac{N}{V}+N_2kT. \tag{705, 17}$$

On using (4) we find

$$F^{\text{int}} = N_1kT\log\frac{N_1}{u_1(T)}+2N_2kT\log\frac{N_1}{u_1(T)}-NkT\log\frac{N}{V}+N_2kT$$
$$= NkT\log\frac{VN_1}{u_1(T)N}+N_2kT$$
$$= NkT\log\frac{V}{V-\tfrac{1}{2}Nv_0}+NkT\log\left\{1-\frac{2NA(T)}{V}\right\}+NkT\frac{NA(T)}{V}, \tag{705, 18}$$

by (7), (13) and (14). Expanding the logarithms and substituting for $A(T)$ from (11), we obtain, correct to terms in $(Nv_0/V)$,

$$F^{\text{int}} = N^2kT\{\tfrac{1}{2}v_0 - A(T)\}/V$$
$$= \frac{N^2kT}{2V}\int_{v_0}\{1-e^{-\epsilon(r)/kT}\}\,4\pi r^2dr$$
$$= N^2\frac{kT}{V}B(T), \tag{705, 19}$$

in agreement with (704, 3).

The average number of molecular pairs with their relative coordinates in the range $d\xi$, $d\eta$, $d\zeta$ is clearly equal to

$$\tfrac{1}{2}N_2 e^{-\epsilon(\xi,\eta,\zeta)/kT}\,d\xi\,d\eta\,d\zeta/A(T), \tag{705, 20}$$

or according to (13)

$$\frac{1}{2}\frac{N^2}{V}e^{-\epsilon(\xi,\eta,\zeta)/kT}\,d\xi\,d\eta\,d\zeta. \tag{705, 21}$$

We see then that to the present approximation of ignoring the simultaneous interaction of any molecule with two or more other molecules

$$W_{AA}(\xi,\eta,\zeta) = \epsilon_{AA}(\xi,\eta,\zeta). \tag{705, 22}$$

To the same degree of approximation it is true for mixtures of different kinds of molecules that

$$W_{AB}(\xi,\eta,\zeta) = \epsilon_{AB}(\xi,\eta,\zeta). \tag{705, 23}$$

The equalities (22) and (23) are not accurate to higher orders of approximation.

**§ 706. The use of the virial.** It is interesting to verify that the formula obtained for the pressure in § 704 is in agreement with the virial theorem of Clausius. We shall quote this theorem without giving its derivation.* If a particle of mass $m$ has a position defined by the cartesian coordinates $x, y, z$, has a speed $c$, and is acted on by a total force with components $X$, $Y$, $Z$, then the virial theorem states that

$$\overline{\Sigma\,\tfrac{1}{2}mc^2} = -\tfrac{1}{2}\overline{\Sigma\,(Xx+Yy+Zz)}, \tag{706, 1}$$

where the bars denote, as usual, time averages and the summation extends over all the molecules.

When this theorem is applied to a perfect gas, that is an assembly of molecules subject to no forces except the pressure exerted by the walls, one can obtain as a special case of (1)

$$\overline{\Sigma\,\tfrac{1}{2}mc^2} = \tfrac{3}{2}PV. \tag{706, 2}$$

* For the derivation under the most general conditions allowable see Milne, *Phil. Mag.* **50**, 409 (1925).

For an imperfect gas in which the mutual potential energy of two molecules a distance $r$ apart is $\epsilon(r)$, one obtains in place of (2)

$$\Sigma\,\overline{\tfrac{1}{2}mc^2} = \tfrac{3}{2}PV + \tfrac{1}{2}\overline{\Sigma r\frac{\partial\epsilon}{\partial r}}. \tag{706, 3}$$

Neither the derivation of (1), nor those* of (2) and (3) from (1), require any knowledge of the actual forms of the averages occurring in these formulae. To make use of these formulae we need to use the distribution laws. For the average kinetic energy of translation we have

$$\Sigma\,\overline{\tfrac{1}{2}mc^2} = \tfrac{3}{2}NkT. \tag{706, 4}$$

The average number of pairs of similar molecules at a distance apart between $r$ and $r+dr$ is, according to (705, 21),

$$\tfrac{1}{2}N^2 e^{-\epsilon/kT}\,4\pi r^2 dr/V. \tag{706, 5}$$

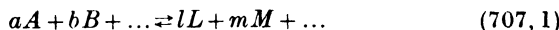
Using (4) and (5), we can transform (3) to

$$PV = NkT - \frac{1}{6}\frac{N^2}{V}\int_0^\infty r\frac{\partial\epsilon}{\partial r}e^{-\epsilon/kT}\,4\pi r^2 dr. \tag{706, 6}$$

On integrating this by parts in such a way that the conditions of convergence at infinity are satisfied and using (704, 1), we find

$$\begin{aligned} PV &= NkT\left\{1 - \frac{1}{2}\frac{N}{V}\int_0^\infty (e^{-\epsilon/kT}-1)\,4\pi r^2 dr\right\} \\ &= NkT\left\{1 + \frac{N}{V}B(T)\right\}, \end{aligned} \tag{706, 7}$$

which agrees with (704, 10).

**§ 707. Chemical equilibria in imperfect gases.** The laws of chemical equilibria for imperfect gases could be deduced by the general method of counting complexions and evaluating averages. This procedure is similar to that used in Chapters II and V, and we shall not give details. The result obtained is simply the usual thermodynamic relations. Thus for the process

$$aA + bB + \ldots \rightleftarrows lL + mM + \ldots \tag{707, 1}$$

the equilibrium condition is

$$a\mu_A + b\mu_B + \ldots = l\mu_L + m\mu_L + \ldots, \tag{707, 2}$$

or abbreviated

$$\Sigma_A\, a\mu_A = \Sigma_L\, l\mu_L. \tag{707, 3}$$

We have only to substitute in (3) the values for the $\mu$'s which we have already obtained.

* For these derivations see *S.M.* p. 287.

If we define the equilibrium concentration product $K_c$† by

$$K_c = \left(\frac{N_L}{V}\right)^l \left(\frac{N_M}{V}\right)^m \cdots \Big/ \left(\frac{N_A}{V}\right)^a \left(\frac{N_B}{V}\right)^b \cdots, \tag{707, 4}$$

we then find by substitution from (704, 5) into (3) that

$$\log K_c = \Sigma_L l \log \phi_L - \Sigma_A a \log \phi_A - \Sigma_L l \Sigma_X \frac{N_X}{V} 2B_{LX}(T)$$
$$+ \Sigma_A a \Sigma_X \frac{N_X}{V} 2B_{AX}(T), \tag{707, 5}$$

where $\Sigma_X$ denotes summation over all types of molecules present, whether or not concerned in the equilibrium. We see thus that $K_c$ is not a constant, but $\log K_c$ varies linearly with the concentrations.

The equilibrium condition can be expressed conveniently in terms of the fugacities $p^*$ defined by (704, 7). We obtain

$$(p_L^*)^l (p_M^*)^m \cdots / (p_A^*)^a (p_B^*)^b \cdots = K_{p^*}, \tag{707, 6}$$

where $$K_{p^*} = (kT\phi_L)^l (kT\phi_M)^m \cdots / (kT\phi_A)^a (kT\phi_B)^b \cdots. \tag{707, 7}$$

$K_{p^*}$ is therefore, unlike $K_c$, a function of temperature only and independent of the pressure.

**§ 708. Some simple models.** The simplest model of a molecule with any pretentions to reality is a rigid sphere of diameter $D$, with no attractive forces between the molecules. This model is defined by

$$\epsilon = +\infty \quad (r < D), \tag{708, 1}$$

$$\epsilon = 0 \quad (r > D). \tag{708, 2}$$

We have therefore

$$B(T) = \frac{1}{2}\int_0^\infty (1 - e^{-\epsilon/kT})\, 4\pi r^2 dr = \frac{1}{2}\frac{4\pi}{3} D^3. \tag{708, 3}$$

For the equation of state we have, according to (704, 10),

$$PV = kT\{1 + \tfrac{2}{3}\pi D^3/V\}. \tag{708, 4}$$

A more useful model is that of rigid spheres of diameter $D$, which attract each other according to some high inverse power of their distance apart. This model is defined by

$$\left.\begin{aligned} \epsilon &= +\infty & (r < D), \\ \epsilon &= \epsilon^*(D/r)^m & (r > D), \end{aligned}\right\} \tag{708, 5}$$

where $m$ is a positive dimensionless constant, usually taken as an integer, and $\epsilon^*$ is the (negative) value of the mutual energy of two molecules in contact.

† Cf. *M.T.* p. 130.

We have therefore by (704, 10)

$$PV = kT\{1+B(T)/V\}, \tag{708, 6}$$

where

$$\begin{aligned} B(T) &= \tfrac{1}{2}\int_0^\infty (1-e^{-\epsilon/kT})\,4\pi r^2 dr \\ &= \tfrac{2}{3}\pi D^3 + 2\pi\int_D^\infty \{1-e^{-\epsilon^* D^m/r^m kT}\}\,r^2 dr \\ &= \tfrac{2}{3}\pi D^3 - 2\pi\int_D^\infty \sum_{\tau=1}^{\infty}\frac{r^2}{\tau!}\left(\frac{-\epsilon^* D^m}{r^m kT}\right)^\tau dr \\ &= \tfrac{2}{3}\pi D^3\left\{1-\sum_{\tau=1}^{\infty}\frac{3}{\tau!(\tau m-3)}\left(\frac{-\epsilon^*}{kT}\right)^\tau\right\}. \end{aligned} \tag{708, 7}$$

Formula (7) is due to Keesom.†

A still more general model has been used by Lennard-Jones. We shall discuss this in §714.

**§ 709. Empirical and semi-empirical equations of state.** The number of empirical or semi-empirical equations of state in use as interpolation formulae is very large.‡ We shall here discuss only three of the simplest, in relation to the theoretical results of the previous section.

The best known practical equation of state is that of van der Waals, namely

$$(P+aN^2/V^2)(V-Nb) = NkT, \tag{709, 1}$$

or

$$(P+a/V^2)(V-b) = kT. \tag{709, 2}$$

Correct to the first power of $b/V$ this is equivalent to

$$PV = kT + \frac{kTb-a}{V}. \tag{709, 3}$$

If we set $a = 0$, this becomes

$$PV = kT\left(1+\frac{b}{V}\right), \tag{709, 4}$$

which is of the same form as (708, 4). Interpreted according to the model of rigid spheres, we see that

$$b = \tfrac{2}{3}\pi D^3, \tag{709, 5}$$

equal to four times the volume $\frac{1}{6}\pi D^3$ of a molecule. If we give the same interpretation to $b$ in the more general formula (3), and compare (3) with (708, 6) and (708, 7), we see that

$$a = kTb\sum_{\tau=1}^{\infty}\frac{3}{\tau!(\tau m-3)}\left(\frac{-\epsilon^*}{kT}\right)^\tau, \tag{709, 6}$$

† Keesom, *Comm. Phys. Lab. Leiden*, Suppl. 24 B, 32 (1912).

‡ See, for example, Kamerlingh Onnes and Keesom, "Die Zustandsgleichung", *Comm Phys. Lab. Leiden*, **11**, Supp. 23 (1912); *Encyk. Math. Wiss.* **5**, no. 10.

so that $a$ is not independent of $T$. Only if we were justified in neglecting all terms of (6) other than the first, should we have

$$a \simeq \frac{3b(-\epsilon^*)}{m-3} = \frac{2\pi D^3(-\epsilon^*)}{m-3}, \tag{709,7}$$

and $a$ would be independent of temperature as supposed by van der Waals. Thus the equation of state of van der Waals, with $a$ and $b$ temperature independent, can be derived only from the following assumptions and approximations:

(1) Rigid spherical molecules of volume $b/4$ attracting each other with a force varying inversely as some power $m+1$ of the distance, the mutual potential energy $\epsilon^*$ of two molecules in contact being $(3-m)a/3b$.

(2) Gas sufficiently dilute to justify our ignoring the simultaneous interaction of a molecule with two or more other molecules.

(3) $-\epsilon^* \ll kT$, so that at all distances of two molecules greater than the distance of contact $(e^{-\epsilon/kT}-1)$ may be replaced by $-\epsilon/kT$.

When the above assumptions are valid, the equation for $PV/kT$ is correct to terms in $1/V$; that is to say, it gives only the first order corrections to the perfect gas equation. As soon as any of the above assumptions and approximations cease to be valid, van der Waals' equation becomes purely empirical.†

The equation of state of D. Berthelot has an appreciably greater range of validity, since it gives a closer representation of the theoretical first order terms. Its usual form is

$$\left(P+\frac{a'}{TV^2}\right)(V-b) = kT, \tag{709, 8}$$

which to the first order is equivalent to

$$PV = kT + \frac{kTb - a'/T}{V}. \tag{709, 9}$$

If we compare this with the theoretical equations (708, 6), (708, 7), and as before identify $b$ with $\frac{2}{3}\pi D^3$, we find instead of (6)

$$a' = kT^2 b \sum_{\tau=1}^{\infty} \frac{3}{\tau!\,(\tau m-3)}\left(\frac{-\epsilon^*}{kT}\right)^{\tau}. \tag{709, 10}$$

The assumption that $a'$ is independent of $T$ may be expected to be fairly near the truth in suitable regions of temperature. For the extra $T$ factor makes it possible for $da'/dT = 0$ for some $T$, whereas for $a$ according to (6) we have always $da/dT < 0$. It would perhaps be better still to use $a'/T^n$ instead of $a'/T$ in (8), with the corresponding changes elsewhere, and adjust $n$ to bring the zero of $da'/dT$ into the most important temperature range.

† Fowler, *Phil. Mag.* **43**, 785 (1922).

Another well-known equation of state is that of Dieterici. It is used empirically in the forms

$$P(V-b) = kT\,e^{-a/kTV}, \qquad (709, 11)$$

$$P(V-b) = kT\,e^{-a'/kT^nV}. \qquad (709, 12)$$

The value of $n$, other than unity, most often used is $\frac{3}{2}$. These equations reduce to

$$PV = kT + \frac{kTb - a'T^{-n+1}}{V}, \qquad (709, 13)$$

correct to terms in $1/V$, agreeing with the equation of state of Berthelot. Dieterici's equations of state are, however, empirically successful over a much wider range of temperature. Though we have here studied only first order corrections, it can be shown that the exponential form of the $a$ or $a'$ correction in Dieterici's equation ought theoretically to be successful over a wider range than the additive form of the $a$ correction in van der Waals' and Berthelot's equations.

For practical use the $a$, $a'$ and $b$ of these and similar equations are often adjusted to give the best fit with the facts over some particular temperature and pressure range, or to reproduce exactly some particular phenomenon such as the critical conditions. It must be remembered that the constants so determined have no direct connection with the intermolecular fields of force, and cannot be used for anything more than a rough qualitative estimate of these fields, or of the sizes of molecules. The mistake of using data from the critical point, for example, for quantitative estimates of molecular diameters has frequently been made. The only correct course is to reduce the observed equation of state to the form

$$PV = kT\left\{1 + \frac{B}{V} + \frac{C}{V^2} + \frac{D}{V^3} + \dots\right\}, \qquad (709, 14)$$

and thus determine the observational value of $B$ as a function of the temperature. Thus determined $B$ can be directly equated to its theoretical value. This is the method followed by Kamerlingh Onnes and Keesom and their collaborators at Leyden, and first correctly applied to the study of intermolecular fields by Keesom. In § 714 we shall give an account of more recent work of this nature, due primarily to Lennard-Jones.

Some authors use a series expansion in powers of $P$ instead of in powers of $1/V$. We can write instead of (14)

$$PV = kT + BP + C'P^2 + D'P^3 + \dots. \qquad (709, 15)$$

The coefficients $B$ are the same in (14) and (15), provided the same unit of volume is used. The coefficients of higher terms are not the same, but are

interrelated by simple algebraic formulae. Another version of the series expansion, sometimes used, is

$$PV = kT\{1+\beta P+\gamma P^2+\delta P^3+\ldots\}, \qquad (709, 16)$$

where

$$B/\beta = C'/\gamma = D'/\delta = \ldots = kT. \qquad (709, 17)$$

Whereas $B$ has the dimensions of volume, $\beta$ has that of a reciprocal pressure or a compressibility. We shall follow Keesom in using the names second, third, fourth, ... virial coefficients for $B, C, D, \ldots$ rather than for $B, C', D', \ldots$ or for $\beta, \gamma, \delta, \ldots$.

In theory it should be possible, if we know the interaction energy, to evaluate $\Omega(T)$ to any desired degree of accuracy, and so to calculate exactly the resulting equation of state. Practically this is a matter of great difficulty and until quite recently very little had been done beyond calculating the second virial coefficient $B$, except for very simple models such as the rigid sphere. It is moreover necessary to calculate many virial coefficients or the equivalent, if any progress is to be made with the rigorous deduction of an equation of state adequate for use near the critical points or at higher densities. Quite recently a considerable advance has been made in this field by Mayer, and we shall give some account of his results in §§ 722–730. The further the accurate study of $\Omega(T)$ is prosecuted, the clearer it becomes that the accurate equation of state cannot be expressed in any simple algebraic form.*

**§ 710. Discussion of intermolecular energies.**† The work of the foregoing sections proceeds on the assumption that the forces between molecules, and therefore the energy terms such as $\epsilon_{\alpha\beta}$, are known, but even now little is known exactly *a priori* about the magnitude of the energies except in the simplest cases of atomic hydrogen and helium. It may some day be possible to derive the energy and so the forces for any atoms or molecules from their electronic structure. But though no difficulties of principle remain, the day still seems distant when such calculations will be a practical possibility. At present we must still rely mainly on indirect methods for such knowledge as we have of intermolecular fields.

The tendency of all molecules to aggregate at low temperatures is sufficient

* Beattie and Bridgman (see especially *Zeit. Phys.* **62**, 95 (1930), where full references are given to earlier papers) have found a useful empirical equation of state approximately valid over the experimental range of temperatures and pressures. This equation contains five adjustable constants. When these constants have been chosen so as to give the best possible fit over a wide range of pressures, it is by no means certain that the equation will give the most accurate value for the second virial coefficient for low pressures. We have therefore made no use of this equation of state.

† §§ 710–720 are based largely on Chapter x of *S.M.*, which was written for the 1st edition by J. E. Lennard-Jones and revised for the 2nd edition by R. A. Buckingham.

indication of the existence of forces of cohesion between molecules, and the very existence of matter leads of necessity to the conclusion that the forces between molecules become repulsive at short distances. Any adequate representations of an intermolecular energy must therefore satisfy these elementary requirements, that its gradient should be positive at great distances and negative at small. Such *a priori* calculations* as have yet been completed naturally confirm this general conclusion. The simplest picture of this kind is that molecules consist of hard impenetrable spheres surrounded by an attractive field. This model we owe to van der Waals. Correctly used it leads to Keesom's formula (708, 7). This model is, however, inadequate to explain the observed compressibility of matter, and for this and other reasons must be discarded (apart altogether from requirements of quantum theory). In general the forces between molecules depend on their relative orientation as well as on their distance apart, but the mathematical difficulties of dealing with such laws of force in theories of the properties of matter are considerable. We shall therefore confine our attention almost entirely to molecules which may reasonably be regarded as spherically symmetrical. The treatment will therefore apply accurately to the inert gases and approximately to such non-polar molecules as $H_2$, $N_2$, $CH_4$. It will not apply, except as a very rough approximation, to molecules such as $H_2O$, and $NH_3$ with permanent electric moments. It is natural that such structures of spherical symmetry should at first have been represented by rigid spheres, for the field, apart from the attractive field, is then completely determined by one parameter—the diameter. This simplicity accounts for its popularity as a molecular model,† but a conglomeration of such rigid spheres in close packing fails to possess the observed properties of ordinary solids or liquids. As we now know *a priori* from quantum theory, rigid spheres with attractive fields outside them are not a very good approximation to the actual forces.

It is convenient, if somewhat artificial, to represent the intermolecular energies by the sum of two terms, one yielding an attraction and the other a repulsion, such that the former dominates at large distances. For convenience we may refer to the former as the *dispersion energy*, and the latter as the *overlap energy*. We shall discuss these in turn briefly, when the significance of these names will appear.

* For a summary of the calculations made for atomic H and He, see Pauling and Wilson, *Introduction to Quantum Mechanics*, pp. 384 *sqq.* (McGraw-Hill, 1936), where references to the original papers are given. A first attack on the *a priori* calculation of the interaction between two hydrogen molecules $H_2$ has been made quite recently by Massey and Buckingham, *Proc. Roy. Irish. Acad.* **14**, Sect. A, no. 3, 31 (1938).

† For a discussion of the diameters of such model molecules, determined by a variety of methods, see Herzfeld, "Grösse und Bau der Moleküle," *Handb. d. Physik*, **22**, Ed. 2 (Berlin, 1934).

§ 711. **Form of dispersion energy.** The true nature of the attraction between two molecules with no permanent electric moment was first properly related to quantum theory by London.* It is due simply to the polarization of each molecule by the other. Even though each molecule is completely symmetrical when described by its average properties, yet it always has some residual electronic motion, which can be thought of in terms of internal oscillations. Such internal electronic oscillations in each molecule induce further oscillations in the other, and as these will always be in phase there is a resultant attraction. The molecular properties involved are the same as those responsible for the dispersion of electromagnetic waves, whence the name *dispersion energy* suggested by London. For a pair of ideal atoms consisting of electrons free to execute simple harmonic oscillations in three directions around a fixed positive charge, London showed by a simple semi-quantal calculation that the dominant term in the dispersion energy is

$$-\frac{3h\nu_0|e|^4}{8\kappa^2}\frac{1}{r^6}, \tag{711, 1}$$

where $\nu_0$ is the frequency of the oscillators, $-|e|$ the charge of the electron, $\kappa$ the constant of the elastic restoring forces, and $r$ the distance between the two molecules. The coefficient of $r^{-6}$ depends on the simple model assumed, and other more exact models lead to a somewhat different coefficient. But it has been shown† that quite generally the leading term in the energy of mutual polarization is of the form $-\mu r^{-6}$, where $\mu$ is a molecular positive constant.

We have already noted that Keesom assumed empirically an attractive energy of the similar form $-\mu r^{-m}$, though he superposed these attractions on a rigid sphere model. We shall therefore assume an energy of attraction of the form $-\mu r^{-m}$, and shall at a later stage set $m = 6$ in accordance with the dominant term of the dispersion energy.

§ 712. **Form of the overlap energy.** The overlap energy of two molecules is so named because it is important only when the orbitals (effective electron orbits) of the two molecules overlap. Its nature according to quantum theory was first explained by Heitler and London.‡ The overlap energy in general can lead either to strong attractions or strong repulsions at short distances, but in many cases the attractive state is inaccessible owing to Pauli's exclusion principle. When it is not so excluded we have the extra possibility of a state of strong binding—the quantal explanation of

* London, *Zeit. Physikal. Chem.* B, **11**, 222 (1930).

† Lennard-Jones, *Proc. Phys. Soc. London*, **43**, 461 (1931), where references to other work will be found.

‡ Heitler and London, *Zeit. Phys.* **44**, 455 (1927).

chemical combination. In studying intermolecular energies in this chapter we are concerned with molecules in which all possible chemical bonds have already been formed, systems for which the overlap energy gives uniquely the necessary repulsions. We now know from quantum theory that the overlap energy *at great distances* can be represented accurately by a formula of the type $R(r)e^{-r/\rho}$, where $R(r)$ is a polynomial containing positive and negative powers of $r$, and $\rho$ is a constant. This form can be derived by a perturbation method. It would be natural therefore to use some such form to represent the potential energy of the repulsions, if such a form were amenable to calculation. Unfortunately, however, it is not very amenable, and we shall continue to use the empirical form $\nu r^{-n}$ (with $\nu$ and $n$ constant), which is more amenable since it allows an explicit calculation of the second virial coefficient. Such an analysis can achieve considerable success in fitting the experimental data, since $\nu r^{-n}$ can always be made to represent the true form fairly well over a limited range of $r$. In § 718 we shall describe briefly some computations made by Buckingham, assuming for the overlap energy the form $Pe^{-r/\rho}$ with $P$ and $\rho$ constants, a form more closely resembling the theoretical form $R(r)e^{-r/\rho}$.

§ 713. **Resultant form of the intermolecular energy.** In view of the foregoing discussion we shall represent the complete intermolecular potential energy by two inverse power terms $-\mu r^{-m}+\nu r^{-n}$ with $m=6$, and the complete specification of the field requires a determination of three more parameters In order that the field may be effectively attractive at large distances and repulsive at small it is necessary that $n>m$. Though such a simple function of the distance cannot adequately represent actual intermolecular fields over all distances, it is the most general that has yet yielded to mathematical treatment, and as we shall see far from inadequate in applications. We shall complete the mathematical analysis before substituting $m=6$.

§ 714. **Theoretical form of second virial coefficient.** Following Keesom we write the equation of state in the form (709, 14) We have then according to (704, 1)

$$B=B(T)=\frac{1}{2}\int_0^\infty (1-e^{-\epsilon(r)/kT})\,4\pi r^2 dr$$

$$=-\int_0^\infty \frac{\partial\epsilon}{\partial r}e^{-\epsilon(r)/kT}\frac{2\pi r^3}{3kT}dr, \qquad (714,1)$$

by integration by parts. In § 708 we evaluated $B$ for rigid spheres of diameter $D$ with an energy of attraction $\epsilon^* D^m/r^m$ for $r>D$, and obtained formula

(708, 7) due to Keesom. We shall now consider the more general mode. with an interaction energy of the form

$$\epsilon = -\frac{\mu}{r^m} + \frac{\nu}{r^n}. \qquad (714, 2)$$

This can be written in the alternative form

$$\frac{\epsilon}{\epsilon^*} = \frac{n}{n-m}\left(\frac{r^*}{r}\right)^m - \frac{m}{n-m}\left(\frac{r^*}{r}\right)^n, \qquad (714, 3)$$

where $r^*$ is the value of $r$ at which $-\epsilon$ has a maximum value equal to $-\epsilon^*$. The parameters $\mu$, $\nu$ in (2) are related to the parameters $\epsilon^*$, $r^*$ in (3) by

$$\mu = \frac{n}{n-m}(-\epsilon^*)\, r^{*m}, \quad \nu = \frac{m}{n-m}(-\epsilon^*)\, r^{*n}. \qquad (714, 4)$$

As $r$ decreases from $\infty$ to $r^*$, the mutual potential energy decreases from zero to a minimum (negative) value $\epsilon^*$. If the two molecules with negligible kinetic energy approach each other from infinity, their kinetic energy will increase to a maximum value $-\epsilon^*$ at $r = r^*$, and will then decrease again, attaining a value zero at a distance $D$ given by

$$\frac{D}{r^*} = \left(\frac{m}{n}\right)^{1/(n-m)} \qquad (714, 5)$$

We may in a sense regard $D$ as an effective collision diameter for slow molecules.

The evaluation of $B$ for this interaction energy has been performed by Lennard-Jones.† He has shown that

$$B = B(T) = \tfrac{2}{3}\pi r^{*3}\left(\frac{m}{n}\right)^{3/(n-m)} F(y) = \tfrac{2}{3}\pi D^3 F(y), \qquad (714, 6)$$

where $$y^n = \left(\frac{\mu}{kT}\right)^n \left(\frac{kT}{\nu}\right)^m = \left(\frac{n}{n-m}\right)^n \left(\frac{n-m}{m}\right)^m \left(\frac{-\epsilon^*}{kT}\right)^{n-m}, \qquad (714, 7)$$

and the function $F(y)$ is defined by

$$F(y) = y^{3/(n-m)}\left\{\Gamma\left(\frac{n-3}{n}\right) - \frac{3}{n}\sum_{\tau=1}^{\infty}\Gamma\left(\frac{\tau m-3}{n}\right) y^{\tau}/\tau!\right\}. \qquad (714, 8)$$

From (7) we see that $-n(\log y)/(n-m)$ differs from $\log T$ only by a function of $n$, $m$ and $\epsilon^*$, and from (6) we see that $\log|F(y)|$ differs from $\log|B|$ only by a function of $n$, $m$ and $r^*$. It follows that, provided values of $m$, $n$ are used, such that the interaction energy is adequately represented by the form (2) or (3), then the theoretically constructed curve representing $\log|F(y)|$ plotted against $n(\log y)/(n-m)$ should be superposable on the experimental curve representing $\log|B|$ plotted against $\log T$. Examples of

† Lennard-Jones, *Proc. Roy. Soc.* A, **106**, 463 (1924). For a condensed summary, see Lennard-Jones, *Physica*, **4**, no. 10, 941 (1937).

curves of $\log|F(y)|$ plotted against $n(\log y)/(n-6)$ are shown in Fig. 1 corresponding to $m = 6$ and the values 8, 9, 12, $\infty$ of $n$.

It is to be noted that all the curves show a maximum except that for $n = \infty$, which corresponds to the rigid sphere, and this curve tends to an asymptote for infinite $-\log y$. The physical interpretation of this is that for hard impenetrable molecules there is always an "excluded volume" however high the temperature, whereas for "compressible" molecules there is an ever-growing interpenetration of the molecular fields as the temperature

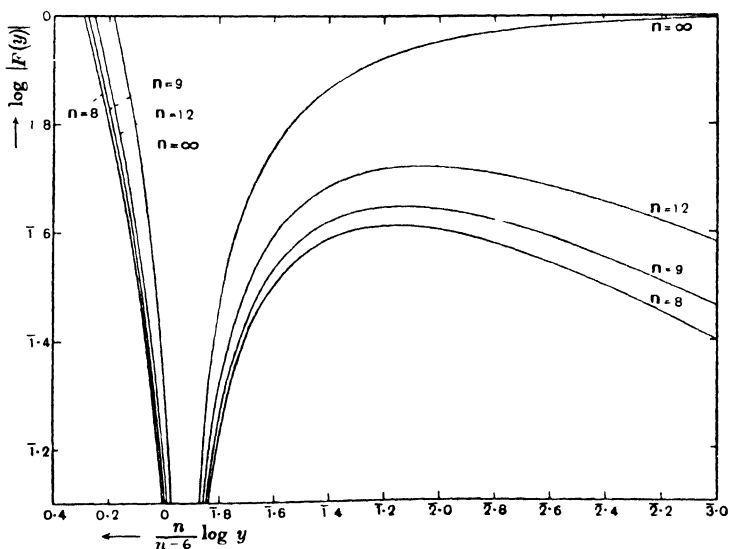



Fig. 1. Theoretical curves from which can be derived the second virial coefficient as a function of $T$, for $\epsilon(r) = -\mu r^{-6} + \nu r^{-n}$.

increases, and since the intermolecular energies at any given compression are finite, the gas tends to become more and more like an ideal gas. As will be shown presently, the observations of $B$ for helium and neon exhibit a maximum and thus exclude the rigid molecular model. It may be regarded as reasonably certain that all other gases would show the same maximum property if the observations could be carried to a high enough temperature.

In the left-hand portion of the curve, corresponding to low temperatures, $F(y)$, and so also $B$, is negative; in the right-hand portion, corresponding to high temperatures, $F(y)$, and so also $B$, is positive. These two portions are separated by the Boyle point at which $B$ is zero. The Boyle point is therefore determined by the equation

$$F(y) = 0. \qquad (714, 8)$$

This equation has been solved for $m = 6$ and various values of $n$ by Devonshire,† and the values of the root, denoted by $y_B$, are given in Table 1. The temperature $T_B$ of the Boyle point can be calculated from $y_B$ by means of (7) and will be proportional to $|\epsilon^*| = -\epsilon^*$. Values of $kT_B/|\epsilon^*|$ are also given in the table.

TABLE 1

*Constants of Boyle point for $m = 6$ and various values of $n$*

| $n$ | $y_B$ | $kT_B/\lvert\epsilon^*\rvert$ |
|---|---|---|
| 9 | 1·140 | 4·58 |
| 10 | 1·119 | 4·07 |
| 11 | 1·100 | 3·71 |
| 12 | 1·082 | 3·43 |

**§ 715. Amagat units of volume.** If the equation of state is written in the form

$$PV = kT\left\{1 + \frac{B}{V} + \frac{C}{V^2} + \ldots\right\}, \tag{715, 1}$$

it is evident that $B$ has the dimensions of $V$, that $C$ has the dimensions of $V^2$ and so on. In our formulae $V$ denotes the molecular volume and the molar volume is $\mathbf{N}V$, where $\mathbf{N}$ is Avogadro's number (the number of molecules in a mole). It is the custom adopted by many experimenters to use for each gas a unit of molar volume such that $\mathbf{N}V = 1$ at 0° C. and 1 atmosphere. These units of volume were introduced by Amagat and are called Amagat units. The Amagat unit varies from one gas to another according to the extent of the deviation from perfection at 0° C. and 1 atmosphere, but this variation is very small and we may take the Amagat unit to be $2{\cdot}24 \times 10^4$ cm.$^3$ for $\mathbf{N}V$ or $3{\cdot}70 \times 10^4$ Å$^3$ for $V$. Amagat units have been used by Kamerlingh Onnes and other workers at Leyden. Other data must be corrected to this scale to obtain comparable values of $B$.

**§ 716. Comparison with experimental data.** If the values of the constants $m$, $n$, $\mu$, $\nu$ were known, one could by means of formulae (714, 6), (714, 7), (714, 8) compute values of the second virial coefficient $B$ for various temperatures, and compare the values so calculated with those obtained from the observed equation of state (715, 1). But as theory predicts only that $m = 6$ but not the values of $n$, $\mu$, $\nu$, all one can do is to examine whether these constants can be so chosen as to fit the experimental data for $B$.

Lennard-Jones'‡ procedure is to construct curves, such as those in Fig. 1, of $\log|F(y)|$ plotted against $n(\log y)/(n-6)$ for different values of $n$, and

† See Lennard Jones, *Physica*, **4**, no 10, 946 (1937).

‡ Lennard-Jones, *Proc. Roy. Soc* A, **106**, 463 (1924)

to examine whether any of these can be superposed on the curve of $\log|B|$ plotted against $\log T$. Examples of this are shown in Fig. 2, which will be discussed below. Having superposed the curve for given $n$ and $m = 6$ on the experimental curve for $\log|B|$ against $T$, the values of $\epsilon^*$, $D$ or of $\epsilon^*$, $r^*$ or of $\mu$, $\nu$ are calculated from the relative positions of the superposed scales, using the formulae (714, 6), (714, 7) and (714, 8). A more accurate method of determination of the best values of $\epsilon^*$, $D$ or of $\mu$, $\nu$, when a suitable value of $n$ has been found, has been used by Buckingham.‡

TABLE 2

*Observed values of the second virial coefficient* B *in Amagat units*

All data due to Holborn and Otto except those marked †
which are due to Nijhoff, Ilin and Keesom

| $T°$ K. | $10^4 B$ in Amagat units | | | | |
|---|---|---|---|---|---|
| | He | Ne | A | $H_2$ | $N_2$ |
| 65·1 | — | −9·35 | | −8·18 | — |
| 71·5 | 4·58† | — | — | — | — |
| 89·9 | 4·81† | — | — | — | — |
| 90·0 | 4·73 | — | — | −2·47 | — |
| 90·5 | — | −3·65 | — | — | — |
| 123 | — | 0·04 | – | 1 31 | |
| 126·5 | 5·53† | — | — | — | — |
| 143 | — | — | — | — | −35 6 |
| 169·7 | 5·89† | — | — | — | — |
| 173 | — | 2·88 | −28·7 | 4·08 | −23·1 |
| 223 | — | 4·06 | −16·9 | 5·39 | −11·8 |
| 273 | 5·29 | 4·75 | − 9·86 | 6·24 | − 4·61 |
| 323 | 5·23 | — | − 4·92 | 6·76 | − 0·11 |
| 373 | 5·10 | 5·29 | − 1·92 | 6·94 | 2·74 |
| 423 | — | — | 0·52 | — | 5·14 |
| 473 | 4·93 | 5·82 | 2·08 | 7·00 | 6·85 |
| 573 | 4·69 | 6·14 | 5·01 | — | 9·21 |
| 673 | 4·54 | 6·12 | 6·83 | — | 10·5 |

The values in this table are taken from Buckingham, *Proc. Roy. Soc.* A, **168**, 264 (1938) as regards He, Ne, A, and from *S M.* p. 303 as regards $H_2$, $N_2$.

Although observations on the isothermals of gases have been accumulating since the classical experiments of Andrews on carbon dioxide,§ a strict comparison of theory and experiment has been possible only since the elaborate analysis of the observational material made by Kamerlingh

‡ See *S.M.* p. 299.

§ For a full account of the earlier literature on equations of state, see Kamerlingh Onnes and Keesom, "Die Zustandsgleichung", *Comm. Phys. Lab. Leiden*, **11**, Supp. 23 (1912); *Encyk. Math. Wiss.* **5**, no. 10.

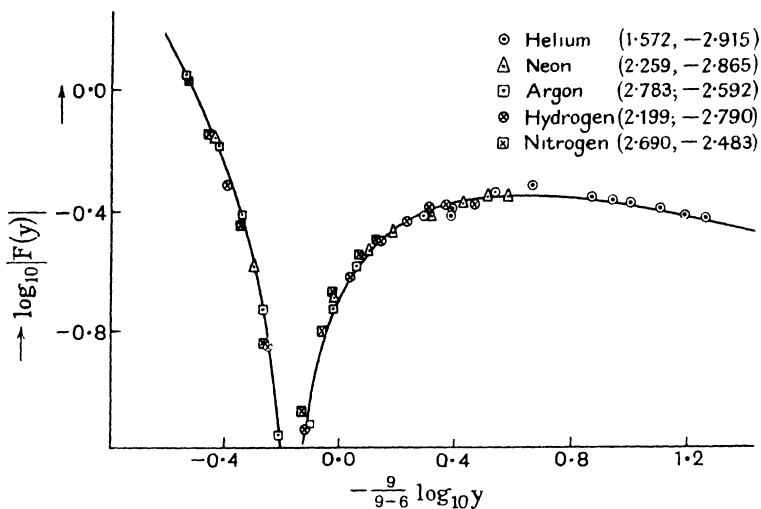



Fig 2*a*. Showing the determination of the interaction constants from the experimental second virial coefficients *n* is taken to be 9 and the numbers in brackets are the values of $\log_{10} T + \frac{9}{9-6} \log_{10} y$ and of $\log_{10}|B| - \log_{10}|F(y)|$ respectively.

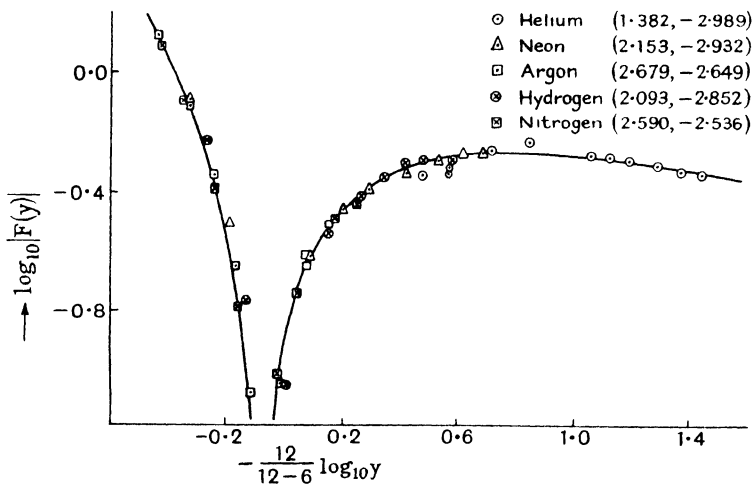



Fig 2*b* Showing the determination of the interaction constants from the experimental second virial coefficients. *n* is taken to be 12 and the numbers in brackets are the values of $\log_{10} T + \frac{12}{12-6} \log_{10} y$ and of $\log_{10}|B| - \log_{10}|F(y)|$ respectively.

Onnes.‡ His method, or slight modifications of it, has since then been adopted by many subsequent workers, and especially by Holborn and Otto,§

TABLE 3

*Intermolecular potential energy constants for gases calculated from experimental equations of state*

The intermolecular energy is

$$\epsilon(r) = -\frac{\mu}{r^6}+\frac{\nu}{r^n} = -\frac{n}{n-6}|\epsilon^*|\left(\frac{r^*}{r}\right)^6+\frac{6}{n-6}|\epsilon^*|\left(\frac{r^*}{r}\right)^n.$$

All energies in ergs; all distances in $10^{-8}$ cm. (Å.).

Values for He, Ne, A obtained by Buckingham, *Proc. Roy. Soc.* A, **168**, 264 (1938). Only for He do these values differ from Buckingham's earlier values given in *S.M.* p. 306. Values for $H_2$, $N_2$ obtained by Lennard-Jones, *Proc. Phys. Soc.* **43**, 461 (1931). Actually Lennard-Jones gives values of the force constants $6\mu$ and $(n-1)\nu$, whereas we give values of the energy constants $\mu$ and $\nu$.

| | $n$ | $\mu\times 10^{10}$ ergs $Å^6$ | $\nu\times 10^{10}$ ergs $Å^n$ | $r^*$ Å. | $D$ Å. | $-\epsilon^*\times 10^{15}$ ergs | $-\epsilon^*/k$ deg. |
|---|---|---|---|---|---|---|---|
| Helium | 8 | 0·0370 | 0·304 | 3·31 | 2·87 | 0·701 | 5·12 |
| | 9 | 0·0237 | 0·510 | 3·185 | 2·78 | 0·755 | 5·51 |
| | 10 | 0·0173 | 0·948 | 3·09 | 2·72 | 0·792 | 5·78 |
| | 12 | 0·01085† | 3·56 | 2·95 | 2·63 | 0·827 | 6·03 |
| | 14 | 0·0076 | 13·9 | 2·84 | 2·56 | 0·823 | 6·00 |
| Neon | 8 | 0·207 | 1·83 | 3·43 | 2·97 | 3·16 | 23·1 |
| | 9 | 0·145 | 3·50 | 3·31 | 2·89 | 3·65 | 26·6 |
| | 10 | 0·114 | 7·32 | 3·22 | 2·83 | 4·11 | 30·0 |
| | 12 | 0·0832 | 35·5 | 3·08 | 2·74 | 4·89 | 35·7 |
| | 14 | 0·0678 | 182 | 2·98 | 2·68 | 5·51 | 40·2 |
| Argon | 8 | 2·37 | 31·5 | 4·21 | 3·64 | 10·7 | 78·2 |
| | 9 | 1·70 | 76·8 | 4·08 | 3·56 | 12·4 | 90·5 |
| | 10 | 1·37 | 205 | 3·97 | 3·50 | 13·9 | 102 |
| | 12 | 1·03 | 1620 | 3·83 | 3·41 | 16·5 | 120 |
| | 14 | 0·867 | 13650 | 3·72 | 3·35 | 18·7 | 136 |
| Hydrogen $H_2$ | 9 | 0·178 | 5·1 | 3·50 | 3·06 | 3·21 | 23·4 |
| | 10 | 0·142 | 11·6 | 3·42 | 3·01 | 3·58 | 26·1 |
| | 12 | 0·105 | 64·9 | 3·28 | 2·92 | 4·25 | 31·0 |
| Nitrogen $N_2$ | 9 | 2·27 | 132·0 | 4·43 | 3·87 | 9·95 | 72·6 |
| | 10 | 1·85 | 393 | 4·34 | 3·82 | 11·1 | 81·0 |
| | 12 | 1·40 | 3700 | 4·17 | 3·72 | 13·25 | 96·7 |

† Owing to a numerical slip the published value was 0·0104. (Private communication from Buckingham.)

who have carried out a series of accurate observations on the inert gases and have presented their results in a form comparable with theory. Their

‡ Kamerlingh Onnes, *Comm. Phys. Lab. Leiden*, no. 71, or *Proc. Sect. Sci. Amsterdam*, **4**, 125 (1902).

§ Holborn and Otto, *Zeit. Phys.* **23**, 77 (1924); **30**, 320 (1924); **33**, 1 (1925); **38**, 359 (1926).

experimental results for several gases, as well as those of Nijhoff, Iliin and Keesom† for helium are collected in Table 2. We have omitted the data for helium at such low temperatures that a classical treatment of the gas is no longer justifiable. The values of $B$ are given in Amagat units.

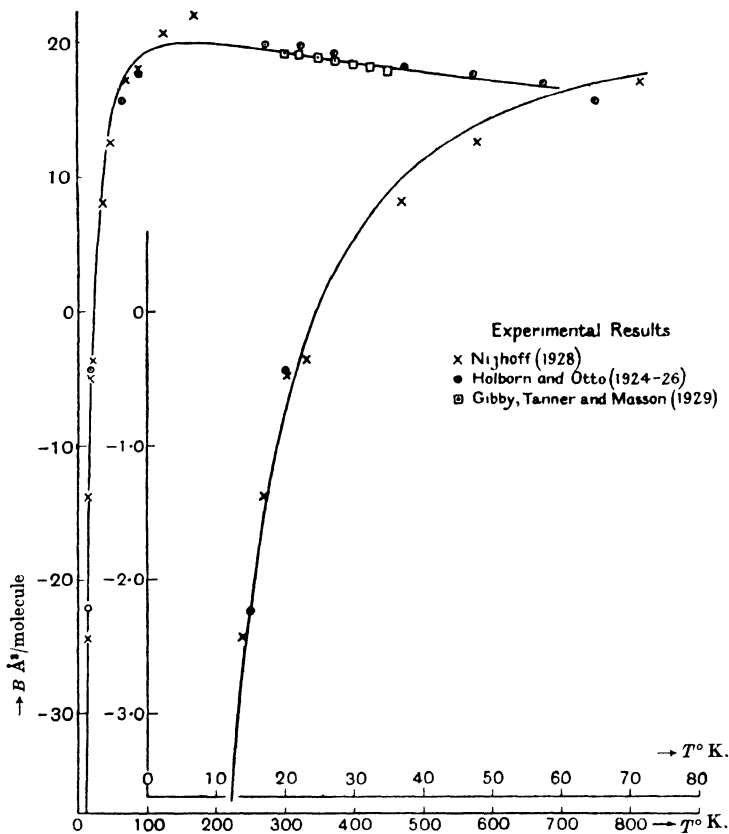



Fig 3. The second virial coefficient as a function of $T$, with observed values for He, for $\epsilon(r) = -\mu r^{-6} + \nu r^{-12}$. $B$ in Å³/molecule

Even when by reference to quantum theory we have fixed $m$ at 6, it does not seem possible to determine $n$, $\mu$, $\nu$ uniquely from the equation of state. A good fit can be obtained over a range of values of $n$ (or $m$ for that matter), but when $m$ and $n$ are fixed the equation of state determines $\mu$, $\nu$ or $\epsilon^*$, $D$ with some precision.[A]

The experimental data for the five gases given in Table 2 can be satis-

† Nijhoff, Iliin and Keesom, *Comm. Phys. Lab Leiden*, no. 188c (1928).

[A] See appendix, § A5.

factorily fitted by any value of $n$ between 8 and 14. In Table 3 are given the best values of the constants $\mu$, $\nu$ and of the alternative constants $\epsilon^*$, $r^*$ or $D$. Any of these sets of values gives a fair representation of the second virial coefficient. The diagrams† in Figs. 2*a* and 2*b* show that the fit is equally good for $n = 9$ or $n = 12$; the diagrams for $n = 8$, 10, 14 are similar. The

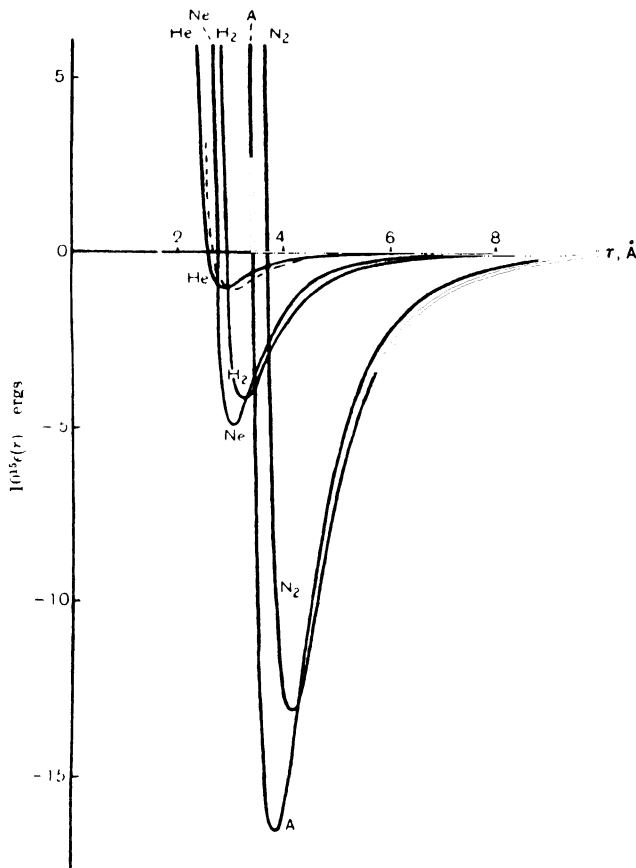



Fig. 4. The mutual potential energies of pairs of inert gas atoms as a function of their distance apart $\epsilon(r) = -\mu r^{-6} + \nu r^{-12}$. The dotted curve shows the calculated value of Slater and Kirkwood.

accuracy of the agreement is shown in Fig. 3, in which the experimental values of $B$ plotted against $T$ are compared with the curve calculated with $n = 12$ and the values of the other constants given in Table 3.

The intermolecular energy so determined is shown as a function of $r$ for the five gases in Fig. 4. The actual curves are there drawn for $m = 6$, $n = 12$.

† We are indebted to Dr C. S. Lu for constructing these diagrams.

It is interesting to compare the curve for He with *a priori* calculations by Slater and Kirkwood* which are shown by the dotted curve. The derived energies are in excellent agreement with the calculated ones.

An alternative method of correlating experimental data with interaction energies is afforded by the Joule-Thomson effect. We saw in § 704 that, in

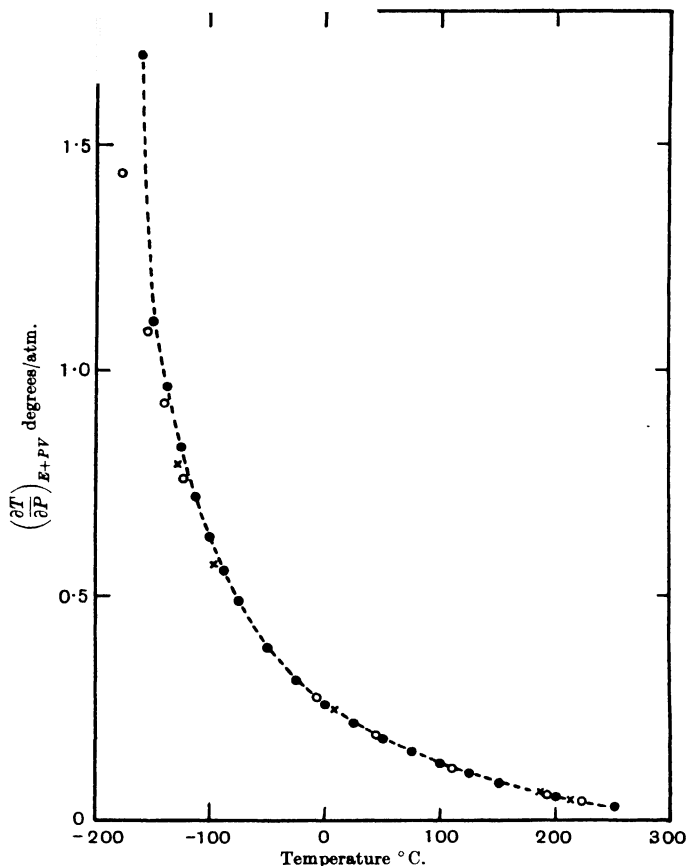



Fig. 5. Nitrogen: Joule-Thomson coefficient extrapolated to zero pressure. ●, experimental observations by Roebuck and Osterberg; ○, calculated, $n = 12$; ×, calculated, $n = 9$.

the limit of low pressures, the Joule-Thomson coefficient is determined by $T$, $c_P$ and $d(B/T)/dT$. For a monatomic gas $c_P = \frac{5}{2}k$ and so an experimental determination of the limiting value of the Joule-Thomson coefficient gives

* Slater and Kirkwood, *Phys. Rev.* **37**, 682 (1931).

an experimental value for $d(B/T)/dT$ at the experimental temperature. If such values are available over a range of temperatures, they can be compared with the values calculated from assumed interaction energies. This method of comparison has been used by Hirschfelder and others.†

In Fig. 5 the experimental values of the Joule-Thomson coefficient, extrapolated to zero pressure, for nitrogen are plotted against the temperature and compared with the theoretical values derived from the interaction energies. The theoretical values have been calculated for $n = 12$ and for $n = 9$ with the values of $\epsilon^*$ and $D$ given in Table 3. The agreement between the experimental data and either set of calculated values is good. Similar good agreement is found for helium and argon. This agreement is not an independent confirmation of the accuracy of the assumed interaction energies, but is rather a confirmation of the thermodynamic consistency of two kinds of experimental data, the $P$-$V$-$T$ data and the Joule-Thomson coefficients.

**§ 717. Gases at high pressures.** As we have already sufficiently emphasized, all our theoretical formulae are applicable only to slightly imperfect gases, because it has proved impossible to calculate any of the virial coefficients other than the second. In this section we shall digress to discuss briefly a formula proposed very recently by Hirschfelder and Roseveare,‡ to express the $P$-$V$-$T$ relations of gases at high as well as low pressures. The formula is certainly not accurate, but it appears to be a useful approximation at least at high temperatures.

Whereas only the second virial coefficient can be calculated for molecules with an interaction energy corresponding to attraction except at small distances, the evaluation of the third virial coefficient for the model of non-attracting rigid spheres has been performed by Jäger, by Boltzmann, by Happel and by van der Waals jr, and that of the fourth virial coefficient by Boltzmann and by Happel.§ The equation of state for this model has the form

$$PV = kT\left\{1 + \frac{b}{V} + \frac{5}{8}\left(\frac{b}{V}\right)^2 + 0{\cdot}2869\left(\frac{b}{V}\right)^3 + O\left(\frac{b}{V}\right)^4\right\}, \qquad (717.1)$$

where $b$ is four times the volume of a rigid spherical molecule, as in van der Waals' equation. The important feature of this model is that all the virial coefficients are independent of the temperature. Hirschfelder and Roseveare suggest that, at least at high temperatures, the values of the third and

† Hirschfelder, Ewell and Roebuck, *J. Chem. Phys.* **6**, 205 (1938). Hirschfelder and Roseveare, *J. Phys. Chem.* **43**, 15 (1939).

‡ Hirschfelder and Roseveare, *J. Phys. Chem.* **43**, 15 (1939).

§ See Happel, *Ann. d. Phys.* **21**, 342 (1906), where references are given to the work of Jäger, Boltzmann and van der Waals jr. The value of the fourth virial coefficient has been confirmed by Majumdar, *Bull. Calcutta Math. Soc.* **21**, 107 (1929). See *S.M.* p. 245 for a general method.

fourth virial coefficients for non-attracting rigid spheres may be useful approximations. They accordingly propose the equation of state

$$PV = kT\left\{1+\frac{B(T)}{V}+0{\cdot}625\left(\frac{b}{V}\right)^2+0{\cdot}2869\left(\frac{b}{V}\right)^3+0{\cdot}1928\left(\frac{b}{V}\right)^4\right\}. \quad (717,2)$$

In this equation the second virial coefficient $B(T)$ is to be calculated according to the theory for the slightly imperfect gas as described in previous sections; the third and fourth virial coefficients have the same values as for a gas of non-attracting rigid spheres. The fifth virial coefficient is assigned a value chosen so that for small values of $V$ the formula may approximate the behaviour of closely packed spheres; the precise physical significance of this assignment of the fifth virial coefficient is not clear to us. The equation of state (2) is thus semi-empirical and it is suggested that it should be a useful approximation for high as well as low pressures, provided the temperature is sufficiently high. It is certainly reasonable to expect the model of non-attracting rigid spheres to be the more useful the higher the temperature. The usefulness of (2) must be decided by comparison with experiment.

The propounders of the equation of state (2) do not give any direct comparison of the observed $P$-$V$-$T$ data with their formula. They do, however, compare calculated and observed values of the Joule-Thomson coefficients of argon over a range of temperatures from 0° C. to 300° C. and of pressures up to 200 atmospheres. The comparison is shown in Fig. 6 and it cannot be denied that the agreement is remarkably good. The parameters $\epsilon^*$ and $D$ used to calculate $B(T)$ were those given in Table 3 for $n = 12$. Apart from these there is the one adjustable constant $b$ in formula (2). The value found to fit the experimental data best is $\mathsf{N}b = 40$ cm.$^3$/mole or $b = 66$ Å.$^3$/molecule. The corresponding value of the diameter $D$ of the rigid sphere is given by $\frac{2}{3}\pi D^3 = 66$ Å.$^3$ or $D = 3{\cdot}1$ Å., whereas the value of $D$ used in the calculation of $B(T)$ is $3{\cdot}4$ Å.

In so far as the equation of state (2) is applicable, we have for the variation of energy with volume at constant temperature

$$\left(\frac{\partial E}{\partial V}\right)_T = -P+T\left(\frac{\partial P}{\partial T}\right)_V = \frac{kT^2}{V^2}\frac{dB(T)}{dT} = \frac{a(T)}{V^2}, \quad (717,3)$$

where $a(T)$ is a function of temperature only. If we integrate (3) we obtain

$$E = E_\infty - a(T)/V, \quad (717,4)$$

where $E_\infty$ is the limiting value of $E$ for large volumes. Equation (4) states that the molecular energy at given temperature varies linearly with the

density: such a relation between energy and density is in fair but by no means exact agreement with experiment especially at high temperatures.

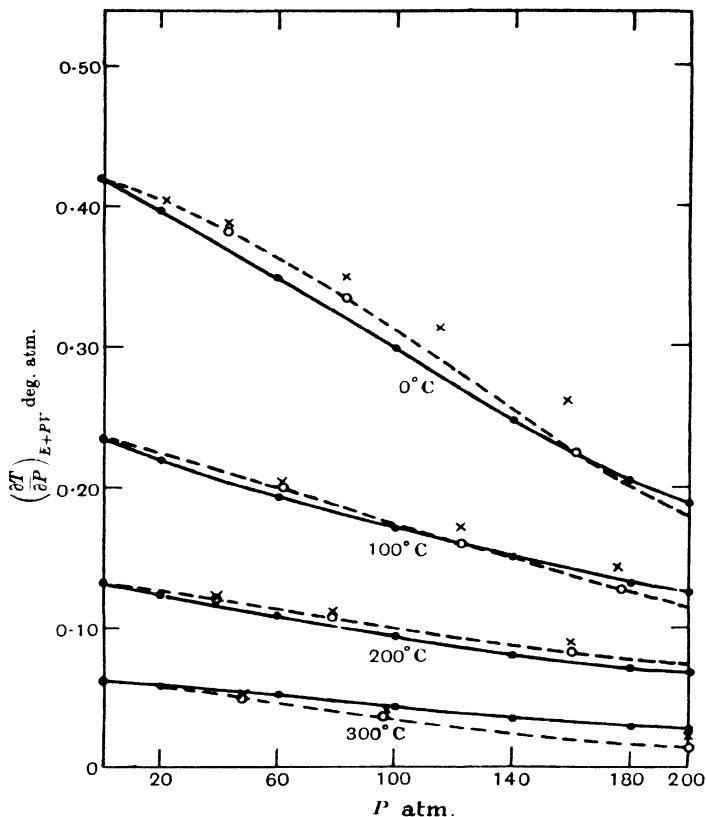



Fig. 6. Argon Joule-Thomson coefficient. ○, calculated, $Nb = 40$ cm.³/mole, ×, calculated, $Nb = 35$ cm.³/mole; ●, observed by Roebuck and Osterberg*.

**§ 718. Analysis of the intermolecular energy.** We have seen that the experimental data for the second virial coefficient $B$ can be accounted for with satisfactory accuracy by assuming an interaction energy of the form

$$\epsilon(r) = -\mu r^{-6} + \nu r^{-n}, \qquad (718, 1)$$

and that for a chosen value of $n$ the values of $\mu$, $\nu$ are fairly precisely determined. Satisfactory agreement can be obtained with any value of $n$ between 8 and 14. The reason is that the main contribution to $B$ comes from a restricted range of values of the intermolecular distance $r$. The form of

* For references see Hirschfelder and Roseveare, *J. Phys. Chem.* **43**, 15 (1939).

interaction (1) is presumably a good approximation over this range of $r$, but we must not expect this form to be accurate either for smaller or for greater values of $r$. To obtain a formula for the intermolecular energy valid over a wider range of $r$ it is necessary to use other considerations such as the properties of the crystal, and such *a priori* approximate calculations of the interaction energy as have been made. Recently Buckingham* has correlated such data with those obtained from the gas, with a view to obtaining more accurate formulae for the interaction energies of helium, neon and argon. We shall summarize Buckingham's conclusions.

According to quantum theory we may expect the overlap energy to be of the form

$$R(r)\, e^{-r/\rho}, \tag{718, 2}$$

where $\rho$ is a constant and $R(r)$ is a polynomial. Calculations by Slater† for helium and by Bleich and Mayer‡ for neon show that an adequate expression may sometimes be obtained if the polynomial $R(r)$ is replaced by a constant. Some confirmation of this, though only over a restricted range of $r$, is given by the work of Born and Mayer§ and by Huggins|| on ionic crystals. This shows that the elastic properties of these crystals are admirably correlated when the repulsive energy of two ions with complete electron shells is represented by a function of the form $Pe^{-r/\rho}$ with $P$ constant.

At large distances the dominant contribution to the interaction is the dispersion energy. According to quantum theory this should have the form

$$-(cr^{-6}+dr^{-8}+\ldots), \tag{718, 3}$$

in which $c, d, \ldots$ are constants. At distances of two molecular diameters or more the only important term is the first. For helium a value for $c$ has been calculated *a priori* from quantum theory by Baber and Hassé.¶

The simplest possible formula for the interaction energy which one can hope may be a good approximation over the whole range of $r$ appears to be

$$\epsilon(r) = Pe^{-r/\rho}-\mu r^{-6}, \tag{718, 4}$$

with $P$, $\rho$, $\mu$ constants. Buckingham has shown that such a form is able to represent with satisfactory accuracy the experimental data both for the gas and for the crystal. The formulae obtained by Buckingham also agree with the scanty *a priori* calculations already mentioned. As it is not practicable to derive an exact analytical value for $B$ from the form (4) of the interaction energy, Buckingham makes use of the results already obtained

* Buckingham, *Proc Roy Soc* A, **168**, 264 (1938)

† Slater, *Phys. Rev* **32**, 349 (1928)

‡ Bleich and Mayer, *J. Chem Phys.* **2**, 252 (1934).

§ Born and Mayer, *Zeit Phys* **75**, 1 (1932)

|| Huggins, *J Chem Phys* **5**, 143 (1937)

¶ Baber and Hassé, *Proc. Camb Phil Soc* **33**, 253 (1937) For a summary of earlier more approximate calculations of this coefficient see Pauling and Wilson, *Introduction to Quantum Mechanics*, p 387 (McGraw-Hill, 1935).

with the intermolecular energy in the form $\epsilon(r) = -\mu r^{-6} + \nu r^{-n}$. The procedure is as follows.

Suppose the virial coefficient $B$ to be known for one particular temperature. Then, if $\mu$ and $n$ are given particular values, $\nu$ is determined uniquely by $B$. The function $\epsilon(r) = -\mu r^{-6} + \nu r^{-n}$ is then an approximate representation of the true potential energy, and will agree with it fairly well over that range of $r$ which contributes most to the integral (714, 1) for $B$. Suppose the same is done for another value of $n$, say $n'$ ($\mu$ being kept unchanged), and another value $\nu'$ of $\nu$ is determined leading to $\epsilon(r) = -\mu r^{-6} + \nu' r^{-n'}$. If now both these functions are plotted against $r$, it seems reasonable to assume that their point of intersection is a point close to the true energy curve. In this way a point is obtained from each measurement of the virial coefficient $B$, and over a wide range of temperature the points are distributed over a curve which should be a close approximation to the true energy. One then examines whether the curve so obtained can be fitted by an equation of the form (4) and one finds that this can be done.

For any assumed form of the interaction energy only a straightforward, though possibly laborious, calculation is required to derive the energy and intermolecular distances of the atoms in the solid for a given type of lattice. The calculated values of the energy and lattice constant can then be compared with the experimental ones.

The interaction energies of the form (4) finally obtained by Buckingham have values of the parameters $P$, $\rho$, $\mu$ given in Table 4. Those for helium are

TABLE 4

*Constants in Buckingham's formula for the interaction energy*

$$\epsilon(r) = -\mu r^{-6} + Pe^{-r/\rho}$$

The unit of length is the Å.

| | $\mu \times 10^{10}$ (ergs Å$^6$) | $P \times 10^{10}$ (ergs) | $\rho$ (Å.) | $N\chi$ (K cal./mole) | | $a$ (Å.) | |
|---|---|---|---|---|---|---|---|
| | | | | Calc. | Obs. | Calc. | Obs. |
| Helium | 0·0147 | 8·71 | 0·216 | — | — | — | — |
| Neon | 0·090 | 25·7 | 0·235 | 0·60 | 0·59 | 3·05 | 3·20 |
| Argon | 1·02 | 169 | 0·273 | 2·00 | 2·03 | 3·76 | 3·81 |

determined largely by the *a priori* quantal calculations already referred to. Those for neon and argon are determined to a greater extent by data obtained from the crystal. The table includes calculated and observed values of the molecular energy of evaporation $\chi$ and of the interatomic distance $a$ in the crystal. The calculated values are strictly the limiting values for $T \to 0$. The agreement is satisfactory and we conclude that the formula (4)

with the constants given in Table 5 is the best representation of the interaction energies of helium, neon and argon consistent with the present state of our knowledge, whether derived from experiment or from theory.

In Figs. 7, 8 the calculated interaction energy is plotted against the interatomic distance. In each case curves are given for an interaction of the type (1) used by Lennard-Jones as well as of the type (4). It is evident that over a restricted range of $r$ the former is a remarkably useful approximation to the latter. This fact encourages the continued use of formulae of the type used by Lennard-Jones, at least as long as the available *a priori* quantal calculations are so sparse. Owing to the great labour involved in accurate calculations dependent on quantum theory, there is no immediate prospect of the position being improved.

**§ 719. Gaseous molecules with electric moments.*** Up to the present we have considered only molecules with no electric moment, so that the attraction is due entirely to the dispersion effect as explained by London. When the molecules have an electric dipole moment there are two other effects superposed on the dispersion effect.

First the dipoles of two molecules tend to orientate each other. The contribution of the orientation effect to the second virial coefficient was calculated by Keesom.† For rigid spheres of diameter $D$ and electric moment $\mu$ he derived the following formula for $B$

$$B = \tfrac{2}{3}\pi D^3\left\{1 - \frac{1}{3}\left(\frac{\mu^2}{D^3kT}\right)^2 - \frac{1}{75}\left(\frac{\mu^2}{D^3kT}\right)^4 - \frac{29}{55125}\left(\frac{\mu^2}{D^3kT}\right)^6 + \cdots\right\}. \tag{719, 1}$$

It is to be noticed that only even powers of $1/T$ occur. The first term is the usual van der Waals' $b$ equal to four times the volume of a molecule. The next term is proportional to $T^{-2}$, not $T^{-1}$ which would be required to give first order agreement with van der Waals' formula.

The second effect is known as the induction effect. More accurately it might be called the effect of primary induction in contrast with the dispersion effect which is secondary induction. It consists simply in the induction of a moment in the one molecule by the permanent moment of the other molecule. This effect has been treated by Debye.‡ The leading term contributed to the second virial coefficient is proportional to $T^{-1}$.

Before the existence of the dispersion effect had been established, attempts had been made to explain the intermolecular attractions entirely by the

* A clear and simple discussion of intermolecular forces has been given by London, *Trans. Fara. Soc.* **33**, 8 (1937). The present section is based on this article.

† Keesom, *Comm. Phys. Lab. Leiden*, Suppl. 24 B, 40 (1912); *Physikal. Zeit* **22**, 129 (1921).

‡ Debye, *Physikal. Zeit.* **21**, 178 (1920); **22**, 302 (1921).

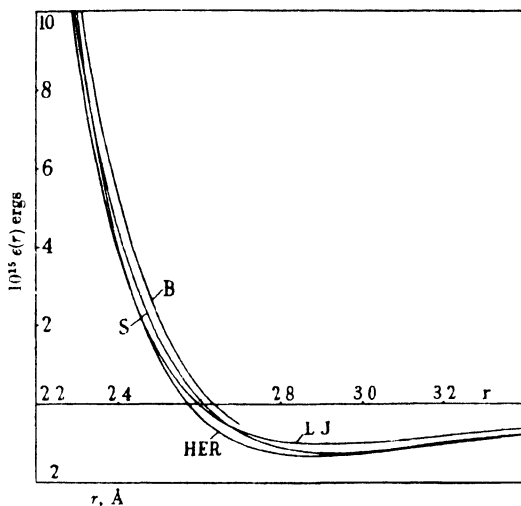



Fig 7 Interaction of helium atoms B Buckingham, $\epsilon(r) = -\mu r^{-6} + Pe^{-r/\rho}$ with values of constants given in Table 4 S Slater, $\epsilon(r)$ of same form as in B and with same values of $\mu$ and $\rho$ but with $P = 7\,7 \times 10^{-10}$ ergs L J Lennard Jones, $\epsilon(r) = -\mu r^{-6} + \nu r^{-12}$ with values of constants given in Table 3 HER Hirschfelder, Ewell and Roebuck, $\epsilon(r)$ of same form as in L J but with different values of the constants

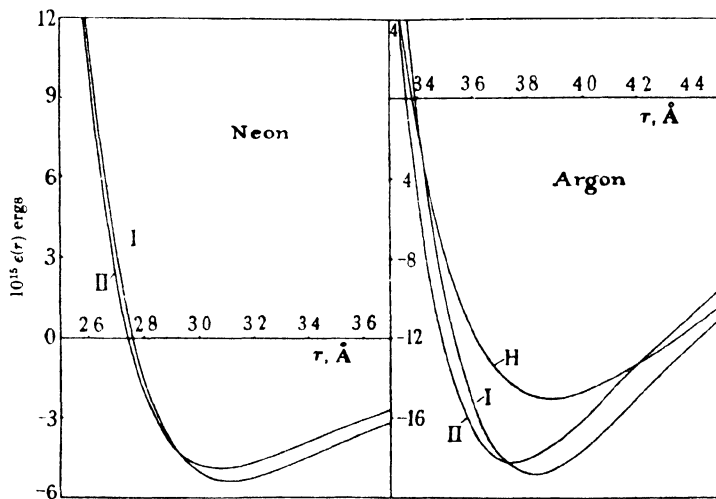



Fig 8 Interaction of neon and argon atoms Curves I $\epsilon(r) = -\mu r^{-6} + Pe^{-r/\rho}$ due to Buckingham, with constants, given in Table 4 Curves II $\epsilon(r) = -\mu r^{-6} + \nu r^{-12}$ due to Lennard Jones, with constants, given in Table 3 Curve H an interaction energy of the form I with constants suggested by Herzfeld and Goeppert-Mayer.

orientation effect and the primary induction of the electric dipoles. When these were found inadequate, further attractions due to electric quadrupoles were postulated. Satisfactory agreement could not be obtained without assuming unreasonably large quadrupoles. It is now known that the attractions are due chiefly to the dispersion effect, the orientation and induction effects being superposed on the dispersion effect for polar molecules. London* has made approximate estimates of these effects which indicate that even for highly polar molecules the dispersion effect is often the most important of the three. The orientation effect can be the most important, but the induction effect has never more than secondary importance. Table 5 due to London shows the relative magnitudes of these effects.

TABLE 5

*The three constituents of the attractive energy*

| | $\mu \cdot 10^{18}$ (e.s.u.) | $\alpha \cdot 10^{24}$ (e.s.u.) | $h\nu_0$ (electron-volts) | Orientation effect $\frac{2}{3}\frac{\mu^4}{kT} \cdot 10^{60}$ (erg cm.$^6$) [$T = 293°$ K.] | Induction effect $2\mu^2\alpha\ 10^{60}$ (erg cm.$^6$) | Dispersion effect $\frac{3}{4}\alpha^2 h\nu_0\ 10^{60}$ (erg cm.$^6$) |
|---|---|---|---|---|---|---|
| CO | 0·12 | 1·99 | 14·3 | 0·0034 | 0·057 | 67 5 |
| HI | 0·38 | 5·4 | 12 | 0·35 | 1·68 | 382 |
| HBr | 0·78 | 3·58 | 13·3 | 6·2 | 4·05 | 176 |
| HCl | 1·03 | 2·63 | 13·7 | 18·6 | 5·4 | 105 |
| $NH_3$ | 1·5 | 2·21 | 16 | 84 | 10 | 93 |
| $H_2O$ | 1·84 | 1·48 | 18 | 190 | 10 | 47 |

In the table $\mu$ denotes the electric moment, $\alpha$ the polarizability and $\nu_0$ the fundamental frequency. The last three columns give the coefficient of $-r^{-6}$ in the statistical average of the mutual attractive potential energy of two molecules distant $r$ apart. Although these absolute values may not be accurate, their relative magnitudes are probably reliable. The respective contributions to the second virial coefficient $B$ will be approximately proportional to these averaged energies of interaction.

§ 720. **Binary mixtures.** Except for the variation of their properties with composition, binary (and higher) mixtures of gases, which do not react chemically, behave like simple gases and no further discussion is required. It does, however, appear desirable to examine the theory of the variation with composition, as curiously erroneous statements have been current.

* London, *Trans. Fara Soc.* **22**, 19 (1937).

For a binary mixture of $N_A$ molecules $A$ and $N_B$ molecules $B$, the equation of state correct to terms in $1/V^2$ is according to (704, 4)

$$P = kT\frac{N_A+N_B}{V}+\frac{kT}{V^2}\{B_{AA}N_A^2+2B_{AB}N_AN_B+B_{BB}N_B^2\}, \quad (720, 1)$$

the $B$'s being given by (704, 1).

If we write

$$N_A = xN, \quad N_B = (1-x)N, \quad (720, 2)$$

so that $x$ is the molecular fraction of $A$ and $1-x$ the molecular fraction of $B$, while $N$ is the total number of molecules, we have

$$P = kT\frac{N}{V}+kT\frac{N^2}{V^2}\{B_{AA}x^2+2B_{AB}x(1-x)+B_{BB}(1-x)^2\}. \quad (720, 3)$$

It is at once obvious that a linear dependence on $x$ must be the exception rather than the rule. The second virial coefficient must in general be a quadratic function* of $x$. It is moreover obvious without explicit calculation that the $n$th virial coefficient must in general be a polynomial of the $n$th degree in $x$. The condition for linearity of the second virial coefficient in $x$ is

$$2B_{AB} = B_{AA}+B_{BB}. \quad (720, 4)$$

There is obviously no reason why this should be satisfied in general, but it is likely to be true or nearly true when the molecular fields are closely similar, for the condition states in a sense that the intermolecular forces between molecules $A$ and $B$ are the mean of those between $A$ and $A$ and between $B$ and $B$. This appears to hold for oxygen-nitrogen mixtures with considerable accuracy,† and was once assumed to hold for helium-neon mixtures for the purpose of deducing the isotherms of pure neon, an assumption shown to be invalid by later work on pure neon.

Verschoyle‡ has established a case of marked failure by the study of hydrogen nitrogen mixtures, which has been discussed theoretically by Lennard Jones and Cook.§ Fig. 9 is taken from their paper and shows the variation of $B$ with composition. From the curve it is clear that the observed points can be fitted reasonably well by a parabola of the theoretical form.

Similar data are available for hydrogen-helium, hydrogen-argon and helium-argon mixtures from the measurements of Masson and his collaborators.‖ Their experimental values of $B$ are shown in Fig. 10. The curves are parabolas with axes parallel to the ordinate axis. It is thus again clear

* Formula (3) was given by Core, *Phil Mag.* **46**, 272 (1923).

† Holborn and Otto, *Zeit Phys.* **23**, 88 (1924)

‡ Verschoyle, *Proc. Roy Soc.* A, **111**, 552 (1926).

§ Lennard Jones and Cook, *Proc. Roy Soc.* A, **115**, 334 (1927).

‖ Gibby, Tanner and Masson, *Proc. Roy. Soc.* A, **122**, 283 (1929). Tanner and Masson, *Proc. Roy. Soc.* A, **126**, 268 (1930).

that a quadratic function of $x$, the mole fraction of one of the components, satisfactorily fits the data. From experimental data such as these we can deduce values of each of the coefficients $B_{AA}$, $B_{AB}$, $B_{BB}$ at the experimental temperatures. This process if continued over a range of temperatures would determine $B_{AA}$, $B_{AB}$, $B_{BB}$ as functions of the temperature. The function $B_{AB}$ could then be dealt with separately, just as $B$ for a single gas, leading

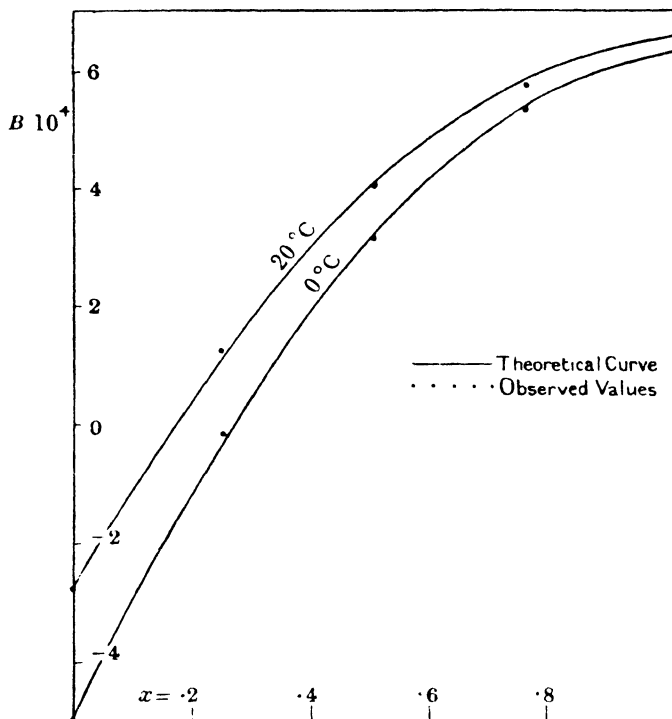



Fig. 9. Variation of the second virial coefficient with composition in hydrogen-nitrogen mixtures. $x$ denotes molecular fraction of $H_2$. $B$ is measured in Amagat units of volume.

to the evaluation of the two constants of the fields between unlike molecules. Unfortunately, there do not appear to be any experimental data sufficiently extensive and accurate for any pair of gases. The work of Verschoyle refers only to two temperatures 0° C. and 20° C. and is thus scarcely adequate. Mixtures of hydrogen and nitrogen have been studied* over the temperature range 0° C. to 300° C. at various pressures up to 1000 atmospheres. Unfortunately the number of observations at pressures below 50 atmospheres

* Wiebe and Gaddy, *J. Am. Chem. Soc.* **60**, 2300 (1938).

is insufficient for an accurate computation of the second virial coefficients, and high accuracy of these coefficients is required if one is to analyse deviations from the additivity relation (4). A detailed experimental study of the *P-V-T* relations of inert gas mixtures in various proportions over a wide

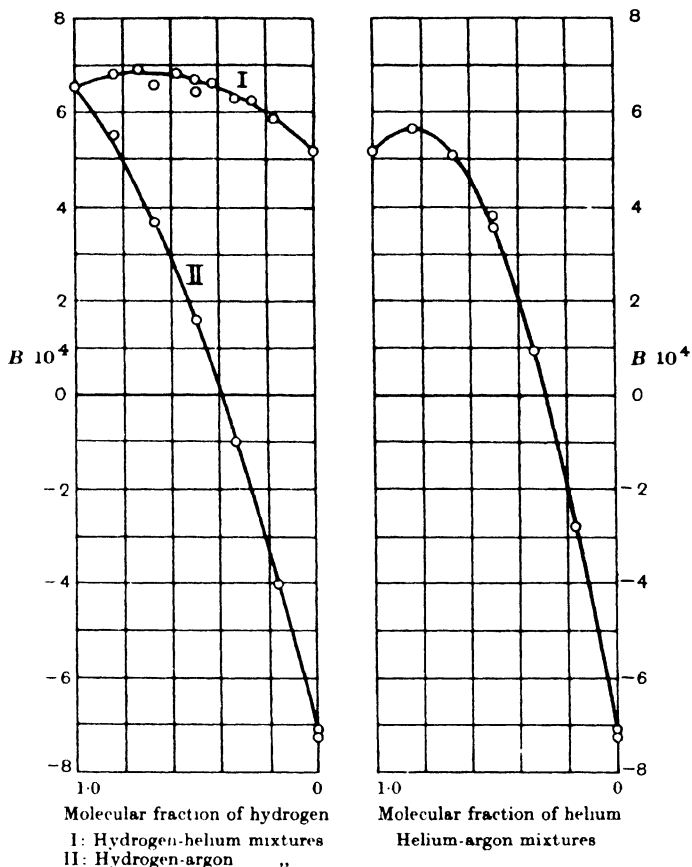



Fig. 10. Second virial coefficient for mixtures at 25° C.
*B* is measured in Amagat units of volume.

range of temperatures and over a pressure range below 50 atmospheres would provide information of great value in the further development of the theory of intermolecular fields.

Quite recently Hirschfelder and Roseveare* have analysed the experimental data for the Joule-Thomson coefficients of mixtures of helium and

* Hirschfelder and Roseveare, *J. Phys. Chem.* **43**, 15 (1939).

nitrogen. It was found possible to obtain good agreement between observed and calculated values of the Joule-Thomson coefficients extrapolated to zero pressure by using interaction energies between two helium molecules or between two nitrogen molecules given in Table 3 for $n = 12$ and by further assuming an interaction energy between a helium molecule and a nitrogen molecule of the same form with suitable values of the parameters. It was assumed that $D$ in the He-$N_2$ interaction energy is equal to the arithmetic mean of the $D$'s in the He-He and the $N_2$-$N_2$ interaction energies and that $\epsilon^*$ in the He-$N_2$ interaction energy is the geometric mean of the

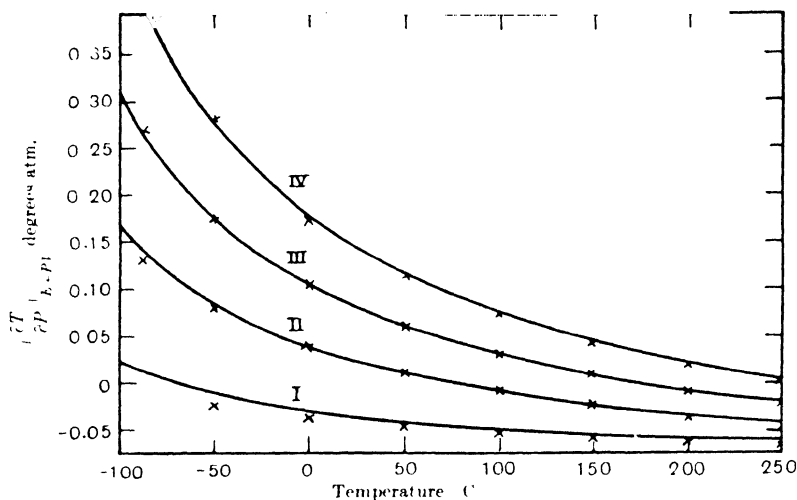



Fig. 11. Helium-nitrogen mixtures. Joule-Thomson coefficients extrapolated to zero pressure. —, experiments of Roebuck and Osterberg, ×, calculated values. Curve I, 75.5 % helium, curve II, 51.0 % helium, curve III, 33.2 % helium, curve IV, 16.6 % helium.

$\epsilon^*$'s in the He-He and $N_2$-$N_2$ interaction energies. This assumed interaction energy for He-$N_2$ leads to values of the Joule-Thomson coefficients represented by the curves in Fig. 11, while the experimental data of Roebuck and Osterberg* are represented by points. The agreement is remarkably good.

§ 721. **Imperfect gases in an external field.** We shall conclude our discussion of slightly imperfect gases by considering briefly the effect of an external field of force in which the potential energy of the molecule of type $A$ is $u_A$. This must not be so large that the approximations we have made become invalid in any part of the assembly. At the densest point ternary encounters must still be negligible. The condition for this is, of course, that if the densest element of the gas in its average state is treated as a separate

* For detailed references see Hirschfelder and Roseveare, *J. Phys. Chem.* **43**, 15 (1939).

assembly, $Nv_0/V$ must still be small there. Then all the distribution laws derived at the beginning of this chapter, while not applicable to the assembly as a whole, will still be applicable to every separate element of the assembly in which $u_A$ may be assumed constant. In each such element the partition function of $A$ will contain the extra factor $e^{-u_A/kT}$. The free energy for that part of the assembly contained in this element will therefore contain the extra terms $\Sigma_A N_A u_A$, and the partial potential $\mu_A$ of $A$ the extra term $u_A$. We have therefore in place of (704, 5)

$$\mu_A = u_A + kT \log \frac{N_A}{\phi_A V} + kT \Sigma_B \frac{N_B}{V} 2B_{AB}(T). \qquad (721, 1)$$

All equilibria involving $A$ are determined by the value of $\mu_A$. In particular the distribution of $A$ between two places is determined by the condition that $\mu_A$ should have the same value.

It is to be noticed that $\mu_A$ is not the *chemical potential*, but the *complete partial potential*. It includes as one term the external potential $u_A$, and it is the remainder that is the *chemical potential** which Gibbs denoted by $\mu_A$.

**§ 722. The general theory of condensation. Introductory.†** So far we have discussed strictly the effect on $\Omega(T)$ and the derived thermodynamic functions only of binary interactions between the molecules of the gas. This allows us to develop $\Omega(T)$ correctly only when terms of the order $(Nv_{\alpha\beta}/V)^2$ and higher orders are negligible compared with unity. But to make any radical advance on this one requires the theory to explain the general qualitative features of the behaviour of gases and liquids, by deriving these features from the properties of $\Omega(T)$. The most striking of these features is the existence of the sharp phase transition, condensation-evaporation, below a critical temperature. This means mathematically that the equation of state of the stable assembly cannot always be represented by one analytic function, but may consist of several analytically different parts. Since the phenomenon of condensation-evaporation is common to all substances, it should be possible to give a general explanation essentially independent of the detailed form of the intermolecular forces. We make no attempt, however, to reach this generality here. We shall be

* In this respect we are departing from the notation of *M.T.* where our present $\mu$ is in Chapter XI denoted by $\mu + m\phi$

† An excellent account of the theory is given by Kahn, Dissertation "On the Theory of the Equation of State" (Utrecht, 1938), an account to which the following sections are much indebted. This dissertation gives full references, and the quantal form of the development as well as the classical. Mayer's work and that of his collaborators, Ackermann and Harrison, is given in *J. Chem. Phys.* **5**, 67, 74 (1937), **6**, 87, 101 (1938). See also Born, *Physica*, **4**, no. 10, 1034 (1937), Born and Fuchs, *Proc. Roy. Soc.* A, **166**, 391 (1938). A key move was made by Ursell, *Proc. Camb. Phil. Soc.* **23**, 685 (1927).

content to continue to make the assumption of § 703, that the intermolecular forces are additive, the total potential energy of a configuration being the sum of the potential energies of all the pairs.

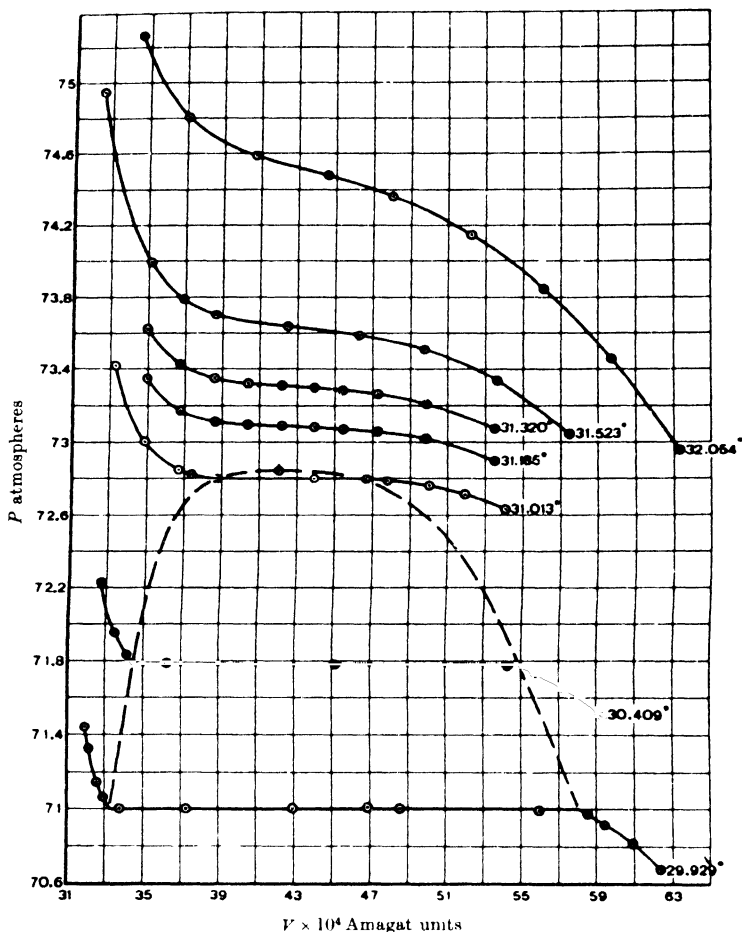



Fig. 12. Pressure-volume relations for carbon dioxide at temperatures near the critical temperature.

Observed isotherms ($P$-$V$ curves at constant $T$) of all vapours divide into two classes according as the temperature lies above or below a critical temperature $T_c$. Examples of each class for carbon dioxide are shown* in Fig. 12.

* From Michels, Blaisse and Michels, *Proc. Roy. Soc.* A, **160**, 367 (1937).

When the volume per molecule is sufficiently large, both classes approximate, as one must expect, to the form for a perfect gas, molecular interactions being then negligible. As the volume per molecule diminishes, the form of the two classes is quite different. When $T > T_c$, there is smooth regular variation along the whole isotherm, which one can express mathematically by saying that it must be represented by a single analytic curve. When $T < T_c$, however, the isotherm consists of three analytically distinct parts, of which the middle one is a horizontal straight line. These parts represent respectively the pure vapour, the saturated vapour in equilibrium with the liquid, and the pure liquid. At each temperature $T < T_c$ there exists a molecular volume $V_s(T)$ at which the vapour isotherm comes sharply to an end, vapour existing only when $V > V_s(T)$ in the vapour. These features must be deduced from the properties of $\Omega(T)$, if further theoretical progress is to be made.

One may perhaps be surprised that this complicated isotherm, which represents the true stable state of the assembly, can be derived from $\Omega(T)$ as given in (703, 1) without further assumptions. Up to the present we have regarded $\Omega(T)$ as giving the free energy of a single homogeneous phase, the free energy of the whole assembly being then constructed by summation of the free energies of the several phases. It would, however, be wrong to assert that one cannot use $\Omega(T)$ to give directly the free energy, and so all the equilibrium properties, of a two-phase assembly. For the integral in $\Omega(T)$ contains in itself all possible configurations of the systems, whether they might be naturally described as corresponding to one homogeneous phase or a division into two or more phases. The free energy which one derives from a correctly evaluated $\Omega(T)$ must correspond to the true state of stable equilibrium of the assembly. No further assumptions can be *necessary.*

One is tempted at first, from the mathematical point of view, to deny that the straightforwardly constructed analytic function $\Omega(T)$ can possibly have such properties. This possibility in fact arises because we are really interested only in the limiting form of $\Omega(T)$ for large $N$. It is only when $N$ is extremely large that the problem has a physical significance. In fact it is not $\Omega(T)$ for fixed $N$ which we require to have these special properties, but rather

$$\operatorname*{Lt}_{N\to\infty} [\Omega(T,V,N)]^{1/N} \quad (T, V \text{ fixed}, V = V/N), \qquad (722, 1)$$

or

$$\operatorname*{Lt}_{N\to\infty} \frac{1}{N}\log\Omega(T,V,N).$$

Even when $\Omega$ is an analytic function of $T$ and $V$ for any fixed $N$, there is no mathematical difficulty in the *limit function* having the required special properties, and in statistical mechanics it is always only these limit functions which are compared with experiments. We shall find other examples of

such discontinuous limit functions occurring in later chapters, many of which are mathematically much simpler than the very complicated function which it is necessary to discuss here.

A further word of warning is desirable. The stable isotherm does not represent all the states of the assembly that are physically realizable. We need only recall the well-known phenomenon of supersaturation, which is represented by a continuation of the vapour part of the isotherm beyond the natural point of condensation. Such states, however, are not true stable states, for their stability can be upset by the catalysing effect of nuclei of condensation, present in numbers that are trivial from the molecular point of view. It is clear that we should not expect to obtain such *metastable* states by the evaluation of (1).

We have explained that the very complicated but direct procedure of correctly evaluating (1) must lead us to the true stable state of the assembly, including the two-phase region, determining in particular the condensation points of the vapour; we have explained further that, to obtain this result, there is no need for any extraneous assumptions, or for the separate discussion of the equilibrium of two-phase assemblies. In practice, however, we almost always discuss phase changes in this very way. We set up expressions which are good approximations to the partition functions for each separate homogeneous phase, derive from them the free energy for each phase, and determine the phase change by minimizing the free energy of the whole assembly, or by the equivalent procedure of equating the partial potentials. There is nothing inconsistent with the arguments of this section in this procedure, nor is the introduction of any extra fundamental hypothesis involved. We are merely in such cases introducing a simplified approximate procedure, which avoids the complicated and perhaps impossible evaluation of $\Omega(T)$ or its equivalent for the whole assembly, by substituting reliable approximate evaluations for separate parts of it, which between them may be expected to cover any term in the exact $\Omega(T)$ which can ever become dominant. This method, as we see in the other parts of this book, is in general completely successful; there is always, however, just a possibility that some finer details of the equilibrium state may get overlooked. It is most important to realize that a phase change can actually be discussed by evaluating $\Omega(T)$ for the assembly as a whole, and we therefore include here a short account of the salient feature of this evaluation, whose success is largely due to the recent work of Mayer.*

**§ 723. The structure of $\Omega(T)$.** We have seen in § 703, that, using the classical approximation and assuming that the intermolecular forces are

* See references on p. 301.

additive, we can write $\Omega(T)$, for a pure fluid of $N$ identical molecules, in the form

$$\Omega(T,V,N)=\frac{1}{N!}\int_{(V)}\cdots\int\prod^{\frac{1}{2}N(N-1)\text{ factors}}(1+\eta_{\alpha\beta})(d\omega)^N, \qquad (723,1)$$

where
$$\eta_{\alpha\beta}=e^{-\epsilon_{\alpha\beta}/kT}-1, \qquad (723,2)$$

$\epsilon_{\alpha\beta}$ being the interaction energy of a pair of molecules. We have assumed further, since no orientational coordinates survive in $\Omega(T)$, that these intermolecular forces are central. Each $\eta_{\alpha\beta}$ differs from zero only when the molecules $\alpha$ and $\beta$ are close together.

The first step in the further evaluation of $\Omega(T)$ is the classification and rearrangement of its various terms. These are all integrals of the various forms

$$\int_{(V)}\cdots\int\eta_{\alpha\beta}\eta_{\gamma\delta}\cdots\eta_{\sigma\tau}\,d\omega_\alpha\ldots d\omega_\tau, \qquad (723,3)$$

multiplied by the relevant powers of $V$. We have so far, in § 703, taken account only of terms such that $\alpha,\beta,\ldots,\sigma,\tau$ all denote distinct molecules. To proceed further we introduce the idea of *a cluster of $l$ molecules*. A cluster is formed by $l$ molecules when each member is so close to at least one other member of the cluster that the corresponding $\eta_{\alpha\beta}$ is significantly different from zero. If we represent a molecule by a dot, and a non-zero interaction by a connecting bar, then —— denotes a cluster with $l=2$, for which the contribution (3) is $\iint_{(V)}\eta_{\alpha\beta}d\omega_\alpha d\omega_\beta$. Similarly $\wedge$ and $\triangle$ are both clusters with $l=3$, for which the contributions are respectively

$$\iiint_{(V)}\eta_{\alpha\beta}\eta_{\beta\gamma}d\omega_\alpha d\omega_\beta d\omega_\gamma, \quad \iiint_{(V)}\eta_{\alpha\beta}\eta_{\beta\gamma}\eta_{\gamma\alpha}d\omega_\alpha d\omega_\beta d\omega_\gamma.$$

Clusters with $l=4$ take any of the forms

[cluster diagrams], ⊠,

and so on.

In the expression (1) for $\Omega$ terms corresponding to clusters of all sizes from $l=1$ to $l=N$ occur. We take a single cluster of $l$ numbered molecules, and form all possible terms $\Pi\eta_{\alpha\beta}$ which make these $l$ molecules a cluster, without interactions with any of the remaining molecules. This product may be more expressively denoted by $\prod\limits_{1\leqslant\alpha,\beta\leqslant l}^{(C)}\eta_{\alpha\beta}$, the $(C)$ denoting that the products are confined to those that make the $l$ molecules a connected cluster. We then form the sum of all these products, all permutations of the molecules being included, and construct the expression

$$b_l=\frac{1}{V\,l!}\int_{(V)}\cdots\int\Sigma\prod_{1\leqslant\alpha,\beta\leqslant l}^{(C)}\eta_{\alpha\beta}\,d\omega_1 d\omega_2\ldots d\omega_l. \qquad (723,4)$$

To these expressions we must add by convention $b_1=1$.

It can then be shown rigorously that $\Omega$ may be expressed fairly simply in terms of the cluster contributions $b_l$. If we form every possible partition of $N$ into clusters of sizes $l$, $l = 1, 2, \ldots, N$, then in any particular partition there will be $n_l$ clusters of size $l$, and $\Sigma_l l n_l = N$. It can then be shown that

$$\Omega(T, V, N) = \Sigma_{(n_l)} \Pi_l \frac{(Vb_l)^{n_l}}{n_l!} \quad (\Sigma_l l n_l = N). \qquad (723, 5)$$

In this expression $\Sigma_{(n_l)}$ means the sum over all possible partitions of $N$, $n_l$ being the number of clusters of size $l$ in each partition.

Still further analysis of the cluster integrals $b_l$ is possible and necessary. In the first place we observe that, though $b_l$ is of physical dimensions $[V]^{l-1}$, it is in fact independent of $V$, when $V$ is sufficiently large. This is one of the essential properties of a cluster in the vapour phase. One of its molecules can be allowed to range over the whole of $V$, but the other molecular centres are then effectively confined to volumes of the order of the size of a molecule in its immediate neighbourhood, owing to the vanishing elsewhere of the $\eta_{\alpha\beta}$ factors. Moreover, when $V$ is sufficiently large, the parts of $V$, in which the ranges of the other molecular centres are restricted by the boundaries of $V$, are negligible. It will happen at times that the important cluster which dominates $\Omega$ contains nearly all the molecules, and then represents the liquid phase, even for such values of $l$, however, $b_l$ will continue to be independent of $V$ so long as $V$ is large compared with the volume of the liquid. We shall restrict the discussion by assuming that $b_l$ is independent of $V$ in what follows. This restriction limits the application of the method that follows to the isotherms of the vapour, and to the saturated vapour and liquid in equilibrium together. We cannot study thus the isotherm of the liquid under higher pressures.

Again the various terms that occur in any $b_l$ are of very different degrees of complexity. In the integrand of $b_3$, for example, there are terms $\eta_{12}\eta_{23}$ and $\eta_{12}\eta_{23}\eta_{31}$. The term $\eta_{12}\eta_{23}$ is of the form

$$\frac{1}{V3!}\int d\omega_2 \int \eta_{12}\, d\omega_1 \int \eta_{23}\, d\omega_3,$$

or

$$\frac{1}{3!}\left[\int \eta_{12}\, d\omega_1\right]^2.$$

It is therefore expressible at once in terms of $b_2$, while the other term $\eta_{12}\eta_{23}\eta_{31}$ does not reduce in this way. We are therefore led to introduce the idea of *irreducible clusters*, which are clusters such that the integrals arising from them are irreducible, in the sense that they do not factorize into the product of simpler integrals of the same form. For example, in $b_3$ the cluster $\wedge$ is reducible, and the cluster $\triangle$ irreducible, as we have already seen.

The essential difference is[A] that in ⋀ one (or more) of the molecules is connected to the rest of the cluster by a single link, while in △ every molecule is connected to the rest by two links at least. In $b_4$ we see similarly that ⌝/, ⊓ are reducible to powers of $b_2$ and ◸ reducible to products of $b_3$ and $b_2$, while □, ⊠, ⊠ are irreducible. The same distinction holds for all values of $l$.

We now therefore construct the expression

$$\beta_j = \frac{1}{Vj!}\int_{(V)}\cdots\int \Sigma^{\mathrm{irr}} \prod^{(C)}_{1\leq\alpha,\beta\leq j+1} \eta_{\alpha\beta}\, d\omega_1 \ldots d\omega_{j+1}, \qquad (723, 6)$$

the terms being those of $b_{j+1}$, but with the summation restricted to the irreducible clusters of $j+1$ molecules, including all possible permutations. It can then be shown that

$$l^2 b_l = \Sigma_{(m_j)} \Pi_j \frac{(l\beta_j)^{m_j}}{m_j!} \quad (\Sigma_j j m_j = l-1). \qquad (723, 7)$$

It is to be noticed that the structures of (4) and (6) are identical, and also those of (5) and (7). We have to imagine in (7) that $l-1$ is partitioned in all possible ways, there being $m_j$ groups of size $j$ in any particular partition; we then form the expression $\Pi_j (l\beta_j)^{m_j}/m_j!$ for each partition, and sum over all partitions.

The combinatory theorem expressed by (6) and (7) is far from simple.

We have thus arrived at an expression for $\Omega$ as a function of functions of the irreducible integrals $\beta_j$, the functional form involved in each step being the same. With a sufficient knowledge of the various $\beta$'s we can determine the necessary properties of $\Omega$. The transformations up to this stage are exact, but the $b$'s and $\beta$'s are independent of $V$ (and $V$), only when $V$ for the whole assembly may be assumed to be sufficiently large. It may be observed again that this restriction does not prevent us from dealing with a condensation process or a highly imperfect gas, a fact which can be made clearer later on, for it is only the volume per molecule in the whole assembly which must be large enough for $b_l$ to be independent of $V$ for the dominant values of $l$.

**§ 724. Integral representation of $\Omega$ and $b_l$.** The expressions for $\Omega$ and $b_l$, which we have just set up, admit of integral representations which are helpful for further progress. If we construct the infinite series

$$\sum_{N=0}^{\infty}\left\{ \sum_{\substack{(n_l)\\(\Sigma_l l n_l = N)}} \Pi_l \frac{(Vb_l)^{n_l}}{n_l!}\right\}\xi^N, \qquad (724, 1)$$

it can be shown that the result of the $N$-summation is to extend the summa-

[A] See appendix, § A6.

tions with respect to the $n_l$ to unrestricted values of the $n_l$. It follows that

$$\sum_{N=0}^{\infty}\left\{\sum_{(n_l)\,(\Sigma_l l n_l=N)} \Pi_l \frac{(Vb_l)^{n_l}}{n_l!}\right\}\xi^N = \exp\left(V\sum_{l=1}^{\infty} b_l \xi^l\right). \tag{724, 2}$$

On using Cauchy's theorem, we deduce from (2) that

$$\sum_{(n_l)\,(\Sigma_l l n_l=N)} \Pi_l \left\{\frac{(Vb_l)^{n_l}}{n_l!}\right\} = \frac{1}{2\pi i}\int_\gamma \frac{\exp\left(V\sum_{l=1}^{\infty} b_l \xi^l\right)}{\xi^{N+1}}\,d\xi, \tag{724, 3}$$

where $\gamma$ is any contour going once counter-clockwise round $\xi = 0$ inside the circle of convergence of the series $\Sigma_l b_l \xi^l$. Equations (3) and (723, 5) give us therefore the comparatively simple formula for $\Omega(T, V, N)$

$$\Omega(T, V, N) = \frac{1}{2\pi i}\int_\gamma \frac{\exp\left(V\sum_{l=1}^{\infty} b_l \xi^l\right)}{\xi^{N+1}}\,d\xi, \tag{724, 4}$$

which may sometimes be more useful in the form

$$\Omega(T, V, N) = \frac{1}{2\pi i}\int_\gamma \frac{\exp\left(N\sum_{l=1}^{\infty} v b_l \xi^l\right)}{\xi^{N+1}}\,d\xi. \tag{724, 5}$$

Exactly similar procedure applied to (723, 7) gives us

$$l^2 b_l = \frac{1}{2\pi i}\int_\gamma \frac{\exp\left(l\sum_{j=1}^{\infty} \beta_j \zeta^j\right)}{\zeta^l}\,d\zeta. \tag{724, 6}$$

We now recall the form of the free energy of the assembly of a set of similar molecules, $N$ in number. By (701, 10) it is of the form

$$\frac{F}{N} = -kT\log\phi(T) - \frac{kT}{N}\log\Omega(T, V, N), \tag{724, 7}$$

which is, more strictly, to be taken in the form

$$\frac{F}{N} = -kT\log\phi(T) - kT \mathop{\mathrm{Lt}}_{N\to\infty}\left\{\frac{\log\Omega(T, V, N)}{N}\right\}. \tag{724, 8}$$

The $\phi(T)$ is the ordinary perfect gas partition function without the volume factor; it depends on $T$ only, and we need take no further account of it here. On the other hand, $\Omega(T, V, N)$ for given $T$ and $V$ can be exhibited as the coefficient of $\xi^N$ in a certain power series. The study of the singularities of the function defined by this power series provides us with a rigorous means of evaluating the free energy.

**§ 725. Rough methods of evaluating $\Omega$.** The discussion of the singularities of the power series just mentioned, required for a rigorous discussion of the value of $\Omega$, is rather complicated. It will therefore be useful to see what results can be obtained by simpler and less rigorous methods, either for an introduction to the rigorous argument, or, if the reader so prefers, as a substitute for it, since the results so obtained are in fact formally correct and tell us what to expect.

*Method* 1. If all the $b_l$ were positive or zero, one would be able to evaluate $\Omega(T, V, N)$ for large $N$ by picking out the maximum term in (723, 5), when the $n_l$ are varied in all possible ways, and equating $\log \Omega$ to the logarithm of this maximum term. This procedure involves therefore finding the values of the $n_l$ which make

$$\Sigma_l n_l \left[ \log \frac{Vb_l}{n_l} + 1 \right]$$

stationary (a maximum), subject to

$$\Sigma_l l n_l = N.$$

We require therefore to make the variation

$$\Sigma_l \delta n_l \log \frac{Vb_l}{n_l}$$

vanish, for all values of $\delta n_l$ subject to the condition

$$\Sigma_l l \delta n_l = 0.$$

It may be shown that this leads to the relations

$$n_l = Vb_l \xi^l, \tag{725, 1}$$

where $\xi$ is the root of

$$\sum_{l=1}^{\infty} l b_l \xi^l = \frac{N}{V} = \frac{1}{v}, \tag{725, 2}$$

and, for the same $\xi$,

$$\log \Omega = V \sum_{l=1}^{\infty} b_l \xi^l - N \log \xi. \tag{725, 3}$$

These formulae are in fact of the correct form, but they cannot be thus established, since the $b_l$ are not all positive.

*Method* 2. The same result is obtained by applying the method of steepest descents to the integral (724, 5). The conditions of applicability of the method are, however, somewhat critical, and, when one examines them in detail, one finds that they must tend to fail as the saturation volume $V = V_s$ is approached. What then happens is that the position of the saddle point on the real axis of $\xi$ tends to move, as saturation is approached, to the point where the circle of convergence of $\Sigma_l b_l \xi^l$ cuts the real axis. Since the $b_l$ are not all positive, this point may not be a singularity of $\Sigma_l b_l \xi^l$, but the

conditions of applicability of the method are destroyed nevertheless. Evaluations made in this way cannot therefore be rigorously used to *establish* the occurrence and position of the points of condensation on a given isotherm.

*Method* 3. Somewhat similar difficulties obstruct an attempt to proceed by constructing the grand partition function for the assembly for given $V$, $T$, $\lambda$. The grand partition function $\Xi(T, V, \lambda)$ for this assembly is, by definition,

$$\Xi(T, V, \lambda) = \sum_{N=0}^{\infty} \Omega(T, V, N)\{\phi(T)\lambda\}^N, \tag{725, 4}$$

summed for all $N$ for given $T$ and $V$; $\phi(T)$ is the usual partition function for one molecule without the $V$-factor, defined in (701, 8). But we have already seen, according to (724, 2), that $\Omega(T, V, N)$ is the coefficient of $\xi^N$ in $\exp(V\Sigma_l b_l \xi^l)$. Therefore

$$\Xi(T, V, \lambda) = \exp\left[V \sum_{l=1}^{\infty} b_l\{\phi(T)\lambda\}^l\right]. \tag{725, 5}$$

It follows at once from the general properties of $\Xi$ that

$$\bar{N} = \lambda \frac{\partial}{\partial\lambda} \log \Xi = V \sum_{l=1}^{\infty} l b_l\{\phi(T)\lambda\}^l, \tag{725, 6}$$

giving $\bar{N}/V$ in terms of $\lambda$, or, by inversion, $\lambda$ in terms of $\bar{N}/V$; it follows also that

$$PV = kT \log \Xi = kTV \sum_{l=1}^{\infty} b_l\{\phi(T)\lambda\}^l. \tag{725, 7}$$

Equation (6) is the same as equation (2) of method 1, with $\xi$ identified as $\lambda\phi(T)$. Equation (7) is the same equation as one derives from (724, 8) and (3) by the use of the standard equation

$$P = -\frac{\partial F}{\partial V} = kT \frac{\partial}{\partial V} \log \Omega.$$

So far as it goes this method is rigorous, but it must, however, assume that $\Sigma_l b_l\{\phi(T)\lambda\}^l$ and $\Sigma_l l b_l\{\phi(T)\lambda\}^l$ converge for all values of $\lambda$ concerned. We may not, without further investigation, assume this convergence in a rigorous treatment of condensation. The results, however, are formally correct for the vapour state.

A rigorous investigation can proceed by studying the radius of convergence of the power series (724, 1), but we cannot attempt to include any account of the mathematics of this difficult method. We must be content instead to state the results of this investigation, which are those of this section somewhat amplified, and to describe their application to the vapour phase and to condensation.

**§ 726. The theoretical isotherms and the condensation point for a vapour.** The results of the complete investigation may be stated as follows. In the vapour

$$PV = kTV\sum_{l=1}^{\infty} b_l\{\phi(T)\lambda\}^l, \tag{726, 1}$$

where $\lambda$ is determined in terms of $V$ and $T$ by

$$\sum_{l=1}^{\infty} lb_l\{\phi(T)\lambda\}^l = \frac{1}{V}. \tag{726, 2}$$

This result we found already in § 725. It can be shown further that (2) and (1) can be replaced respectively by

$$\phi(T)\lambda = \frac{1}{V}\exp\left(-\sum_{j=1}^{\infty}\beta_j\frac{1}{V^j}\right), \tag{726, 3}$$

$$PV = NkT\left[1-\sum_{j=1}^{\infty}\frac{j}{j+1}\beta_j\frac{1}{V^j}\right]. \tag{726, 4}$$

These formulae in terms of the $\beta$'s are exact consequences of the $(b, \beta)$ relations given in (723, 7) or (724, 6). The $(\Omega, b)$ relations and the $(b, \beta)$ relations are strictly parallel in form, but the $(\Omega, b)$ relations are required only in an asymptotic form for large $N$, and may be studied in a provisional way (though not rigorously) as in § 725, while the $(b, \beta)$ relations, leading to (3) and (4), are required in an exact form, and can be obtained only by arguments of considerable depth. Formula (3) is in fact the result of the inversion of power series (2), and (4) the result of substituting (3) into (1).

Equation (4) is the simplest possible form of the virial expression for the isotherm of a vapour, in terms of the irreducible cluster integrals. Further study is directed primarily towards determining the range of validity of (4), or the corresponding expression for $\Omega$. This shows that, for any temperature, there may or may not exist a saturation volume $V_s$ such that (4) holds for $V \geq V_s$, while for $V < V_s$

$$PV_s = NkT\left[1-\sum_{j=1}^{\infty}\frac{j}{j+1}\beta_j\frac{1}{V_s^j}\right]. \tag{726, 5}$$

The pressure is then constant and the free energy $F$ must then be a linear function of $V$. This is exactly what we require to represent the phase change of condensation.

**§ 727. The dependence on the temperature.** The investigation, which we have just sketched, derives the essential features of the condensation process and of a one or two-phase system directly from the properties of $\Omega(T, V, N)$ in the desired manner. The investigation, however, is hardly complete without an investigation of the dependence of $V_s$ on $T$, and of the form of the isotherms as functions of $T$. This part of the

*investigation*, however, is more difficult, as one must know more about the *behaviour of the $\beta$'s and $b$'s. One should be able to prove, for example, that* as $T$ increases $V_s(T)$ diminishes until $T$ reaches a critical value $T_c$, above which temperature $V_s$ no longer exists. These properties, however, have not yet been strictly derived by study of the $b$'s and $\beta$'s as functions of $T$ given by (723, 4) and (723, 6). One can only see that the expected physical properties are mathematically possible, and that it is reasonable to expect them to be true. Further than this one cannot yet proceed rigorously.

There are, however, features which may be important, in the form of the isotherms of the vapour ($V \geqslant V_s(T)$), which can already be established. The condensation point $V_s$ may appear on any given isotherm for either of two reasons. It turns out that $V = V_s$ has to be the end of the vapour isotherm, either if $z = 1/V_s$ is a singularity of the function $\Sigma_l b_l z^l$, or if $\Sigma_j j\beta_j(1/V_s)^j = 1$. The actual value $V_s$ for any isotherm will be the larger of the values of $V$ required by these alternative conditions, and, so far as one can say *a priori*, one of these conditions might determine $V_s$ in one temperature range, and the other in another range. When $V_s$ is fixed by the condition

$$\sum_{j=1}^{\infty} j\beta_j \frac{1}{V_s^j} = 1, \qquad (727, 1)$$

we see by differentiating (726, 4) that

$$\left(\frac{\partial P}{\partial V}\right)_T = -\frac{kT}{V^2}\left[1 - \sum_{j}^{\infty} j\beta_j \frac{1}{V^j}\right]; \qquad (727, 2)$$

it follows from (1) and (2) that at the condensation point

$$\left(\frac{\partial P}{\partial V_s}\right)_T = 0. \qquad (727, 3)$$

On the rest of the isotherm

$$\left(\frac{\partial P}{\partial V}\right)_T < 0 \quad (V > V_s), \qquad (727, 4)$$

or else the condensation point would have come sooner by earlier satisfaction of (1). When, on the other hand, $1/V_s$ is fixed as a singularity of $\Sigma_l b_l z^l$, we must have

$$\left(\frac{\partial P}{\partial V}\right)_T < 0 \quad (V \geqslant V_s) \qquad (727, 5)$$

It is possible therefore, and physically it is a plausible arrangement, that we shall find the isotherms arranged as follows:

(1) $T > T_c$. $V_s$ does not exist.

$$\left(\frac{\partial P}{\partial V}\right)_T < 0.$$

(2) $T_c > T > T_m$. $V_s$ exists. $\Sigma_j j\beta_j(1/V_s)^j = 1$.

$$\left(\frac{\partial P}{\partial V}\right)_T < 0 \quad (V > V_s): \quad \left(\frac{\partial P}{\partial V_s}\right)_T = 0.$$

(3) $T_m > T$. $V_s$ exists. $\Sigma_j j\beta_j(1/V_s)^j < 1$.

$$\left(\frac{\partial P}{\partial V}\right)_T < 0 \quad (V \geqslant V_s).$$

When the isotherms are arranged thus, we have a transition at $T = T_c$ from a real $V_s$ for which $\Sigma_j j\beta_j(1/V_s)^j = 1$ to the case where a real $V_s$ does not exist. This must be expected to occur when the real root $y = 1/V_s$ of $\Sigma_j j\beta_j y^j = 1$ becomes a double root and then complex. It follows therefore that in this case $\Sigma_j j^2\beta_j(1/V_s)^j = 0$, and therefore that

$$\left(\frac{\partial P}{\partial V_s}\right)_{T=T_c} = 0, \quad \left(\frac{\partial^2 P}{\partial V_s^2}\right)_{T=T_c} = 0. \qquad (727,6)$$

This is the ordinary criterion defining the critical point in the inexact customary theory.

It will be clear to the reader, from this short account of recent studies of $\Omega$, that much more remains to be done, especially in the study of $\Omega(T)$ as a function of temperature. We hope, however, that in spite of this, the present account will suffice to show how a rigorous discussion can and must proceed, and the general type of results that one may expect to obtain from it. In particular we observed the possibility, entirely overlooked by the customary discussion, that there may be, at a temperature below the critical temperature, a distinct subsidiary but nevertheless important change in the nature of the isotherms. It is as yet uncertain whether this change of type actually occurs, and what would be its physical meaning if it did. It is possible that this temperature might be a temperature above which a supersaturated state is impossible. Any such suggestion is, however, quite uncertain. We are not yet even sure whether in fact $T_m$ will ordinarily occur with intermolecular forces of the type that are actually found.

Another point which arises is that the isotherms in the neighbourhood of the critical point may possibly be non-analytic. The conventional study of this neighbourhood is given in the following section. Deductions are made from the assumption that the isothermal $P$-$V$ relation in this neighbourhood may be represented by a family of analytic curves depending on one parameter $T$, with the unstable parts cut out, when they occur, by horizontal straight lines drawn according to a rule of equal areas. One can see at once, from the more profound discussion of the foregoing sections, that the assumption that the isotherms are a family of analytic curves thus modified

is not necessarily true, and need not even be a close approximation to the truth. Deductions drawn in the customary manner from this assumption must therefore be used with caution.

**§ 728. Customary discussion of the critical point and the properties of the isotherms in its immediate neighbourhood.** The foregoing analysis of $\Omega(T, V, N)$ has become available only within the last year (1938), and even so has hardly reached a stage at which it is suitable for practical applications. In default of such accurate methods, it has been customary in the past, and must still remain customary for many years to come, to use approximate methods for determining the existence of the critical point, and for studying the isothermals in its neighbourhood, of a type which we shall now describe in detail.

We set up, usually by a violent extrapolation of equations approximately valid for a nearly perfect gas, a family of analytic curves

$$P = P(V, T). \qquad (728, 1)$$

To be of value as isotherms such a family of analytic curves is chosen so that there exists a critical temperature $T_c$, such that

$$\frac{\partial P}{\partial V} < 0 \quad (T > T_c), \qquad (728, 2)$$

$$\frac{\partial P}{\partial V} = 0 \quad (V = V_1, V_2,\ T < T_c). \qquad (728, 3)$$

In all cases $\partial P/\partial V < 0$ for very small and very large values of $V$. It follows at once that, when $T = T_c$, there exists a critical volume $V_c$ such that

$$\frac{\partial P}{\partial V} = 0, \quad \frac{\partial^2 P}{\partial V^2} = 0 \quad (T = T_c,\ V = V_c), \qquad (728, 4)$$

while $V_1$ and $V_2$ tend to $V_c$ as $T$ tends to $T_c$ from below. In the region $V_1 < V < V_2$, $\partial P/\partial V > 0$, so that the curve cannot represent a physically possible isotherm. It is assumed, however, that for large $V(> V_2)$ the curve does represent the stable (or perhaps only metastable) vapour isotherm, and for small $V(< V_1)$ the stable (or perhaps only metastable) liquid isotherm. The actual condensation or evaporation point, that is the point of transition between the stable liquid and vapour isotherms, may be fixed by a rule, which we discuss on the next page.

It is desirable at this point to examine closely the tacit assumptions which underly this procedure. Since $P = -\partial F/\partial V$, in setting up equations (1) we have really assumed that we have constructed the free energy function (for example statistically) as a function of $T$ and $V$, and that this $F$ has a partial differential coefficient with the properties specified. In the region where

$\partial P/\partial V > 0$ it is recognized that such an $F$ cannot be the true $F$ belonging to the equilibrium state for such a volume and temperature, but it is assumed that the $F$ so constructed corresponds, even in these regions, to the free energy which the assembly would have, if it could be constrained to remain in a single homogeneous phase through this region. We note in passing that the accurate investigation of the nature of $F$ statistically constructed, given in the preceding sections, does not justify any such interpretation, nor the assumption that $F$, if it could be so constructed and evaluated, would be an analytic function of $V$ and $T$.

If, however, we allow the assumption that for all values of $T$, $V$ there is a free energy $F$ for the assembly, constrained to remain a single-phase assembly, then the method introduced by Gibbs* leads to an unambiguous answer as to when such a single phase would split, if allowed to do so, into two phases. In particular we can apply this method to show that at a given temperature, if on any part of the continuous isotherm $\partial P/\partial V > 0$, then at least this part will be unstable, and splitting into two phases will occur. We can also determine, for such a temperature, at what pressure this splitting occurs. In the range of pressures, for which $\partial P/\partial V$ can be positive on the analytic curve, we choose a definite pressure $P$ and denote the smallest value of $V$ for this $P$ by $V'(P)$ and the largest by $V''(P)$; the thermodynamic argument† then tells us that the pressure $P$, at which splitting into two phases occurs, is determined by the relation

$$\int_{V=V''(P)}^{V=V'(P)} V(P)\,dP = 0, \qquad (728,5)$$

the path of integration being along the analytic curve for the given temperature. The pressure $P$ thus determined is the equilibrium pressure for the two-phase liquid-vapour assembly at the given temperature; $V'(P)$ is the molecular volume of the liquid under the pressure of its vapour, and $V''(P)$ that of the saturated vapour. Equation (5) states that $P$ is fixed by the condition that, in the $(P, V)$ diagram, the two areas enclosed between the analytic single-phase isothermal and the horizontal condensation line have areas numerically equal (but of opposite sign). The condition is consequently known as a *rule of equal areas*.

The approximate nature of this whole method of study of the condensation problem, and of the neighbourhood of the critical point, should be now sufficiently clear. It must not, however, be thought that the weaknesses here stressed affect the thermodynamic discussion of two-phase equilibria which we use freely in other parts of this book. So long as we can construct

* Gibbs, "Representation by surfaces of thermodynamic properties", *Collected Works*, **1**, 33 (Longmans, 1928); van Rijn van Alkemade, *Zeit. Physikal. Chem.* **11**, 289 (1893).

† See *M.T.* p. 60.

statistically accurate thermodynamic functions for each phase for the range of variables in question, then the phase equilibrium deduced thermodynamically is accurate, and remains always as accurate as the statistical construction of the functions. It is only in the neighbourhood of a critical point, near which one possible phase disappears, that a more fundamental treatment of the whole assembly, whether of one or two phases, may be essential.

**§ 729. Further details of the isotherms near the critical point.** We recall shortly some further familiar consequences of the equations of § 728.

The coordinates of the critical points of the family (728, 1) are completely determined by the equations

$$P = P(T, V), \quad \partial P/\partial V = 0, \quad \partial^2 P/\partial V^2 = 0. \qquad (729, 1)$$

These equations determine $P_c$, $T_c$, $V_c$, and it is frequently useful to express the isotherms in the *reduced variables* $\varpi = P/P_c$, $\theta = T/T_c$, $v = V/V_c$, when they become

$$\varpi = \varpi(\theta, v),$$

which is called *the reduced equation of state*, and may take a specially simple form.

By using the approximate theory of § 728 we can determine the dependence on temperature, in the neighbourhood of the critical temperature, of the volume $V^G$ of the saturated vapour at which condensation starts, and the volume $V^L$ of the liquid at which condensation ends.* The formula so obtained for $(V^G - V^L)$ as a function of $(T_c - T)$ is of interest in the theory of surface tension and will be used in § 1018; but the formula itself, depending as it does on § 728, is necessarily unreliable.

If the isothermals near the critical point, including the unstable portions, are a family of analytic curves, then, since $\partial P/\partial V = 0$, $\partial^2 P/\partial V^2 = 0$ at the critical point, and $\partial^3 P/\partial V^3 \neq 0$, the curves in this neighbourhood take the form

$$P = P(T, V) = P_c - (T_c - T)\left(\frac{\partial P}{\partial T}\right)_c - (T_c - T)(V - V_c)\left(\frac{\partial^2 P}{\partial T\, \partial V}\right)_c + \tfrac{1}{6}(V - V_c)^3\left(\frac{\partial^3 P}{\partial V^3}\right)_c, \qquad (729, 2)$$

and terms of higher order, which will be negligible sufficiently near the critical point. The surviving coefficients are necessarily not zero, and their signs are definite. It can be shown that, if the family is to be arranged like

* We use $V^G$, $V^L$ in place of the more precise, but unnecessarily cumbrous $V^G_s$, $V^L_s$.

actual isotherms, then

$$\left(\frac{\partial P}{\partial T}\right)_c = \alpha > 0; \quad \left(\frac{\partial^2 P}{\partial T\,\partial V}\right)_c = -\gamma, \ (\gamma > 0); \quad \left(\frac{\partial^3 P}{\partial V^3}\right)_c = -\beta, \ (\beta > 0).$$

The approximate equation for $P$ then reduces to

$$P = P_c - \alpha(T_c - T) + \gamma(T_c - T)(V - V_c) - \tfrac{1}{6}\beta(V - V_c)^3. \qquad (729, 3)$$

For suitable values of $P$ this equation in $V$ has three real roots, $V_1 < V_2 < V_3$. We now wish to determine $P_0$ for any $T$, where $P_0$ is the pressure at which condensation and evaporation takes place at this temperature according to the approximate theory of § 728. We therefore have to satisfy (728, 5); this is equivalent to satisfying

$$\int_{V_1}^{V_3} P\,dV = P_0(V_3 - V_1), \qquad (729, 4)$$

the roots $V_1$ and $V_3$ being then the molecular volumes $V^L$ and $V^G$ of the liquid and vapour phases respectively at this temperature. On inserting (3) into (4), we find that

$$P_0 = P_c - \alpha(T_c - T) + \tfrac{1}{2}\gamma(T_c - T)(V_3 + V_1 - 2V_c)$$
$$- \tfrac{1}{24}\beta[(V_3 - V_c)^2 + (V_1 - V_c)^2](V_3 + V_1 - 2V_c). \qquad (729, 5)$$

The first approximation to $P_0$ is therefore

$$P_0 = P_c - \alpha(T_c - T), \qquad (729, 6)$$

and to this approximation the roots of (3) are the roots of

$$\tfrac{1}{6}\beta(V - V_c)^3 - \gamma(T_c - T)(V - V_c) = 0,$$

that is

$$V_1 = V_c - \left(\frac{6\gamma}{\beta}\right)^{\frac{1}{2}}(T_c - T)^{\frac{1}{2}}, \quad V_2 = V_c, \quad V_3 = V_c + \left(\frac{6\gamma}{\beta}\right)^{\frac{1}{2}}(T_c - T)^{\frac{1}{2}}. \qquad (729, 7)$$

We can now establish the form of $V_3 - V_1$, that is $V^G - V^L$, for this neighbourhood. We find from (7) that

$$V_3 - V_1 = V^G - V^L = 2\left(\frac{6\gamma}{\beta}\right)^{\frac{1}{2}}(T_c - T)^{\frac{1}{2}}. \qquad (729, 8)$$

This leads, to the same approximation, to

$$\frac{1}{V^L} - \frac{1}{V^G} = 2\left(\frac{6\gamma}{\beta}\right)^{\frac{1}{2}}\frac{(T_c - T)^{\frac{1}{2}}}{V_c^2}. \qquad (729, 9)$$

If the molecules are of mass $m$, then $1/V = \rho/m$, where $\rho$ is the density of the phase, and we have

$$(\rho^L - \rho^G)^2 = \frac{24m^2\gamma}{\beta}\frac{T_c - T}{V_c^4}. \qquad (729, 10)$$

For any chosen empirical equation of state, such as van der Waals' or Dieterici's, $\beta$ and $\gamma$ can be explicitly calculated.

A further property of the liquid and vapour volumes, which can be derived from (7), is that

$$V_3 + V_1 = V^G + V^L = 2V_c. \qquad (729, 11)$$

To the same approximation this may be written

$$\rho^G + \rho^L = 2\rho_c, \qquad (729, 12)$$

where $\rho_c$ is the density at the critical point. Equation (12) is the simplest possible form of *the rule of the rectilinear diameter*, which states that, as an empirical fact,

$$\rho^G + \rho^L = \lambda + \mu(T_c - T) \quad (\lambda, \mu \text{ const.}). \qquad (729, 13)$$

The form (13) is remarkably well obeyed by many liquids. Since by letting $T \to T_c$ it follows that $\lambda = 2\rho_c$, the determination of the rectilinear diameter fixes $\rho_c$ and therefore $V_c$; in fact this is the most reliable observational method of determining $V_c$.

# CHAPTER VIII

## LIQUIDS AND SOLUTIONS OF NON-ELECTROLYTES

**§ 800. Introduction. Normal and associated liquids.** It has long been customary to classify liquids into two classes called *normal liquids* and *associated liquids*, but the rules for such a classification cannot be rigidly defined. Originally the classification was a purely experimental one. For the majority of liquids, particularly organic liquids, it was noticed that many of their physical properties, such as vapour pressure, surface tension, viscosity, obeyed at least roughly certain empirical rules. Amongst these we need name only Trouton's rule, which will be discussed in later sections. These liquids were termed *normal liquids*. But there was found to be a large minority of liquids whose properties did not fit these empirical rules. These liquids were called *associated liquids*, because the deviations from the empirical rules were believed to be due to association of the molecules found in the vapour to form larger molecules in the liquid. It was noticed in particular that the majority of substances containing hydroxyl or amino groups form liquids belonging to the associated group. With the accumulation of data it soon became possible, from a knowledge of the chemical structure of a molecule, to predict whether it would form a normal or an associated liquid. Our knowledge of the structure of liquids, though still meagre, has greatly increased of recent years through the application of X-ray analysis, and the study of optical and electrical properties. We are now able to give a fairly satisfactory definition of a normal liquid in terms of molecules. A liquid will be normal if the internal degrees of freedom of each molecule are not seriously disturbed by the close proximity of the other molecules in the liquid. Such a liquid may then be treated as an assembly whose partition function will be the product of a partition function for the translations of the molecules and partition functions for the internal degrees of freedom of each single molecule, the latter being very similar to those for gaseous molecules. In an associated liquid on the other hand the originally gaseous molecules interact so intimately that the rotational degrees of freedom and perhaps some of the vibrational degrees of freedom are seriously modified; some rotations may become frozen, and atoms from different molecules may become bound to each other so tightly that one speaks of the formation of new chemical links.

As far as normal liquids are concerned our present view of their structure is much the same as it was when the term normal was first used, but the old view of an associated liquid as composed of double or triple molecules,

which themselves behaved normally, is too simple a generalization. The structure of associated liquids can differ from that of normal liquids in several alternative ways, of which the association of two or more gaseous molecules to form larger molecules in the liquid is by no means the most important. These alternatives have been discussed by Bernal* and we shall briefly refer to his conclusions.

On a purely geometrical basis we may consider associated liquids as produced, whenever the molecules of the liquid can be attached to each other by forces which are directed in space and localized in a definite part of the molecule. No liquid in which there exist only the undirected and unlocalized forces of van der Waals or of metallic character has been found to be associated. The type of association will depend on the number of effective links that can be formed by each molecule. If there is only one, the association will be of the simple kind containing a bimolecular complex, as in most monohydric alcohols. If there are two, the association will either be in closed rings, such as may occur in hydrofluoric acid, or in open chains. The two types will differ widely in character; the liquid formed of rings will behave as a normal liquid of higher molecular weight, that formed of chains as a highly viscous, possibly liquid-crystalline aggregate. The change from ring to chain may be promoted by rise of temperature; liquids such as sulphur, which increase in viscosity with heating, belong to this category. If the number of effective links is three or more, the association extends throughout the whole liquid. In such cases, of which water is typical, we have an associated liquid in which there are no intermediate aggregates between the individual molecule and the whole mass of the liquid. Such liquids will tend to have anomalous thermal expansion, high viscosities, and low surface tension. They are most liable to supercooling and readily form glasses. Most of the liquids which are usually called associated fall in this category. It is the number of effective rather than potential links that determines the character of the liquid. Thermal motion diminishes this number, and consequently the degree of association; so does pressure. All liquids near the critical temperature are probably unassociated. This accounts for the anomalies in heat capacity and in thermal expansion which are common in associated liquids.

The nature of the links which exist in associated liquids is gradually becoming clearer. For substances liquid at ordinary temperatures they are predominantly hydrogen bonds. For substances melting at high temperatures, co-valent bonds such as the S—S bond in liquid sulphur or the Si—O—Si bond in molten silicates. Dipole moments other than those due to hydrogen do not usually lead to association, because they are not localized

* Bernal, Address to the Chemical Society, unpublished (1938).

on the surface of the molecule. A certain part may also be played by resonance forces similar to those giving rise to molecular compounds in aromatic crystals, but this has not been studied in liquids.

The function of hydrogen in liquid association has been studied in greatest detail in water, and also in less detail in alcohols and acids. In water the effective number of hydroxyl bonds can be determined from the X-ray diffraction and Raman spectra, which have now been quantitatively explained. The maximum number, four, is found only in ice. In water from 0° to 100° it varies from three to two. All alcohols, and more recently some acids, have been shown by Raman spectra to possess hydroxyl or hydrogen bonds.

The study of associated liquids has as yet barely started. We can form a general picture, but so far relatively few associated liquids have been examined by modern methods, nor have we as yet any quantitative theory of the anomalous properties of associated liquids. It is only to normal (unassociated) liquids that it has been possible up to the present to apply statistical mechanics in a quantitative, or at least semi-quantitative, way. We shall therefore in this chapter be concerned almost entirely with normal liquids.

Even when we exclude association there are incomparably greater difficulties in applying statistical mechanics to a liquid than to a dilute gas or to a crystal. For in a dilute gas we have almost complete randomness of configuration and in a crystal we have almost complete order; in a liquid we have neither and it is this fact which makes it so difficult to find a useful model. It is only quite recently that any progress has been made at all.

Until recent years all attempts to discuss the structural configurations of a liquid have been based on van der Waals' description of a liquid as not essentially different from a gas except that it is more highly compressed Formally this is correct, and there is no absolute discontinuity between these two states of matter. But practically there is an important difference, which can be described as follows. It will be remembered that in van der Waals' treatment of an imperfect gas one of the two corrections introduced into the equations for perfect gases is the replacement of the total volume $V$ by an effective free volume $V-Nb$. Now the treatment of imperfect gases occupying most of Chapter VII, and in fact every satisfactory treatment, except the very recent treatment of Mayer referred to in §§ 722 *sqq*., involves amongst others the assumption that $Nb \ll V$. This means that the free volume is not greatly different from the total volume and the gas is only slightly imperfect. Now in liquids we have the opposite condition $(V-Nb) \ll V$; even at the critical point $(V-Nb) \simeq \frac{1}{2}V$. The simplest possible useful model of a liquid is therefore a collection of spheres, packed not tightly, but not

very far from tightly. This state of affairs, at least in liquids with symmetrical molecules, has been confirmed by X-ray analysis. We are therefore driven to the conclusion that a liquid is much more like a crystal than like a gas, and the structure which we shall accept as the most plausible for a liquid is conveniently referred to as quasi-crystalline. Whereas in a crystal each molecule is surrounded by a definite invariable number of nearest neighbours, this number is not definite in a liquid. Nevertheless, at temperatures well below the critical temperature, the number of nearest neighbours has a fairly well-defined average value, and, although there are fluctuations about this average, these fluctuations are not serious, and the geometrical relationship of each molecule to its immediate neighbours is on the average very similar to that in a crystal. Moreover, the fluctuations are not sufficiently serious to disturb the regularity of the geometrical relationship between immediate neighbours for more than a rather unimportant fraction of centres in the liquid. The fluctuations or occasional irregularities in the configurations of immediate neighbours are, however, usually sufficient to destroy completely any regularity between the configurations of distant molecules. Exceptions can occur, for example with very long molecules, and these lead to anisotropic liquids sometimes called liquid crystals.

**§ 801. Free energies of imperfect gas or liquid.** We showed in Chapter VII that the free energy of an assembly of $N$ molecules of mass $m$ confined to a volume $V$ is given by

$$F = -NkT\log\frac{(2\pi mkT)^{\frac{3}{2}}}{h^3} - NkT\log j(T) - kT\log\Omega(T), \quad (801,1)$$

where $j(T)$ denotes the partition function for all the internal (including rotational, vibrational, electronic and nuclear spin) degrees of freedom, and $\Omega(T)$ is defined by

$$\Omega(T) = \frac{1}{N!}\int\ldots\int e^{-W/kT}(d\omega)^N. \quad (801,2)$$

Here $W$ denotes the configurational potential energy of the assembly (omitting the internal energy of the molecules), referred to a zero with the molecules at infinite separation, and $(d\omega)^N$ denotes the product of the $N$ elements of volume, to which the centres of the $N$ molecules belong. The multiple integration extends over the whole positional phase space accessible to the molecules, and the factorial removes multiple counting of physically indistinguishable configurations. We recall that for a perfect gas $W = 0$ when all the $N$ molecules are inside the specified accessible volume $V$, and $W = \infty$ when any one or more of the molecules is outside this volume. Under these conditions formula (2) reduces to

$$\Omega(T) = V^N/N!. \quad (801,3)$$

We also recall that for a gas only slightly imperfect a satisfactory approximation to $\Omega(T)$ is

$$\Omega(T) = \frac{V^N}{N!}\{1+\xi+O(\xi^2)\}^N, \qquad (801,4)$$

where

$$\xi = \frac{1}{2}\frac{N}{V}\int (e^{-\epsilon_{\alpha\beta}/kT}-1)\,d\omega. \qquad (801,5)$$

In equation (5) $\epsilon_{\alpha\beta}$ is the mutual potential energy of the pair of molecules $\alpha$ and $\beta$, and the integration extends over all possible relative configurations of the two molecules, or alternatively over those configurations where $\epsilon_{\alpha\beta}$ differs appreciably from zero. The approximation (4) is valid only if the deviations from ideality are small, that is if $\xi \ll 1$. When this condition does not hold, it is in principle still possible to find expressions for $\Omega(T)$ in terms of power series in $N/V$, and this procedure was referred to briefly in §§ 722 *sqq*. We saw that the method is exact, the only approximations being made for mathematical convenience, but it is laborious and unlikely at present to be an effective method for the practical study of highly compressed gases or of liquids. There is, however, an entirely different method of evaluation of $\Omega(T)$, though only an approximate one, which has been developed with much success by Lennard-Jones and Devonshire. This method will be described in some detail in §§ 808–812 Before proceeding to details it seems desirable to consider the conditions for the validity of (1), quite apart from the possibility of finding a useful approximation to $\Omega(T)$.

The first condition for the validity of (1) is the separability of the motion of the assembly into the internal motions of the molecules, which contribute $j(T)$, and the translational motion of the individual molecules relative to one another. The second condition is that the translational degrees of freedom of the molecules should be classical. This condition is required in order that it may be possible to separate the energy into a kinetic and a potential part; in the contribution of the translational degrees of freedom to $F$ the term $-kT\log\Omega(T)$ may then be separated from the first term in (1). The third condition for the validity of (1) is that the whole volume $V$ should be available to every molecule of the assembly, except, of course, in so far as the overlap energy included in $W$ prevents two molecules from overlapping. All these conditions are usually at least approximately satisfied by highly compressed gases and even by normal liquids, except hydrogen and helium whose translational degrees of freedom will not be classical at low temperatures. We may therefore regard formulae (1) as of general applicability to normal liquids (except possibly hydrogen and helium) as well as to gases. From this point of view the distinctions between a normal liquid, a compressed gas and a dilute gas are entirely due to differences in

$\Omega(T)$. This will appear more clearly later when we discuss the approximations used by Lennard-Jones and Devonshire to evaluate $\Omega(T)$ for compressed gases and for liquids.

**§ 802. Some crude models of a liquid.** Before describing the more successful attempts at a quantitative evaluation of $\Omega(T)$, it will be profitable to consider some greatly over-simplified models. These models, though much too crude to give accurate quantitative results, are, however, adequate to give the qualitative or even semi-quantitative behaviour of liquids and highly compressed gases.

We recall the model described in § 708 of rigid spherical molecules of diameter $D$ with no attractive forces between the molecules. This model led to the formula for slightly non-ideal gases

$$\Omega(T) = \frac{V^N}{N!}\left(1 - \frac{Nb}{V}\right)^N, \tag{802, 1}$$

where $b = \frac{1}{2}\frac{4\pi}{3}D^3$ is equal to four times the volume of a single molecule regarded as a rigid sphere. We may write (1) in the equivalent form

$$\Omega(T) = e^N(V - b)^N, \tag{802, 2}$$

where $V = V/N$ is the volume per molecule. We may roughly describe $(V-b)$ as the average volume accessible to a single molecule, or the free volume per molecule. Formulae (1) and (2), with the specified value of $b$, were derived only for small deviations from ideality. However, for the assumed model of rigid spheres without attractions, (2) will remain formally correct at any degree of compression, provided that we regard $b$ no longer as a molecular constant but as a function of $V$. We should then find for the assumed model at any degree of compression

$$\Omega(T) = e^N\{v(V)\}^N, \tag{802, 3}$$

where $v(V)$ denotes the free volume per molecule.

The model just considered has little practical interest because it takes no account of the attractions between molecules. A crude, and yet useful, approximation* is obtained by replacing $W$ in (801, 2) by its value averaged over all accessible configurations. Since this value, for samples of liquid in a given physical state, will evidently be proportional to the number of molecules in the same and will be negative, we denote it by $-N\chi$. On this approximation each molecule is thought of as moving freely in a uniform potential $-\chi$, which is a smoothed value for all relative configurations of the given molecule and its neighbours. Since the attractions are supposed

* Guggenheim, *Proc. Roy. Soc* A, **135**, 181 (1932).

short range ones, only near neighbours will contribute appreciably to $-\chi$. The value of $\chi$ will then be determined by the average number of near neighbours at specified distances from a given molecule, and this in turn will be determined mainly by the number of molecules per unit volume, or by its reciprocal $V/N = V$. We may therefore, to this approximation, regard $\chi$, as well as $v$, as a function of $V$ only. This model leads then to the formula

$$\Omega(T) = e^N\{v(V)\}^N e^{N\chi(V)/kT} = \{ev(V)\,e^{\chi(V)/kT}\}^N. \qquad (802,4)$$

We shall for convenience refer to this model and the formulae belonging to it by the name *smoothed potential model*.

The weakness of this model is that no account is taken of the change in the interaction energy as a molecule moves about its average position. Accepting the quasi-crystalline structure of liquids, we can obtain a fairly obvious improvement on the smoothed potential model. We suppose that there are $N$ positions of minimum potential energy $-\chi_0(V)$ in the quasi-crystalline liquid, and that each molecule moves about a position of minimum potential energy in a field corresponding to an isotropic three-dimensional harmonic oscillator of frequency $\nu$, both $\chi_0$ and $\nu$ being regarded as determined by $V$. If $r$ denotes the distance from a position of minimum potential energy, a molecule at this distance will have a potential energy $-\chi_0 + \frac{1}{2}m(2\pi\nu)^2 r^2$. This leads to a better approximation for $\Omega(T)$,

$$\begin{aligned}\Omega(T) &= e^{N(\chi_0+kT)/kT}\left[\int_0^\infty e^{-\frac{1}{2}m(2\pi\nu)^2r^2/kT}\,4\pi r^2\,dr\right]^N \\ &= e^{N(\chi_0+kT)/kT}\left[4\pi\left\{\frac{kT}{\frac{1}{2}m(2\pi\nu)^2}\right\}^{\frac{3}{2}}\int_0^\infty e^{-\xi^2}\xi^2\,d\xi\right]^N \\ &= \left\{e^{(\chi_0+kT)/kT}\left(\frac{kT}{2\pi m\nu^2}\right)^{\frac{3}{2}}\right\}^N. \end{aligned} \qquad (802,5)$$

The model just discussed is essentially due to Mie.* We shall for brevity refer to this model as the *harmonic oscillator model*.

We can now substitute from the alternative formulae (4) and (5) into (801, 1) to obtain expressions for the free energy. We thus obtain for the smoothed potential model, using (4),

$$\frac{F}{N} = -\chi(V) - kT\log\frac{(2\pi mkT)^{\frac{3}{2}}\,v(V)}{h^3} - kT - kT\log j(T), \quad (802,6)$$

and for the harmonic oscillator model, using (5),

$$\frac{F}{N} = -\chi_0(V) - 3kT\log\frac{kT}{h\nu(V)} - kT - kT\log j(T). \qquad (802,7)$$

* Mie, *Ann. Phys.* **11**, 657 (1903).

Formulae (6) and (7) correspond to different models, and both are only rough approximations. The two models should not be confused. For any given values of $T$ and $V$ the formulae for the two models can be made to agree with each other by equating $\chi$ with $\chi_0$ and assigning to $v$ the value

$$v = \left\{\frac{kT}{2\pi m\nu^2}\right\}^{\frac{3}{2}}, \tag{802, 8}$$

but the two formulae cannot be made to agree completely over a range of temperatures, if $v$ and $\nu$ are to be functions of $V$ only. Formula (8) gives an *effective* free volume, when we use the harmonic oscillator model. Conversely if we use the smoothed potential model, we can define an *effective* frequency $\nu$ by

$$\nu = \left(\frac{kT}{2\pi m}\right)^{\frac{1}{2}} v^{-\frac{1}{3}}, \tag{802, 9}$$

so that this $\nu$ is equal to the frequency with which a molecule would travel back and forth between opposite faces of a cube of volume $v$ if its kinetic energy in that direction is $\frac{1}{2}m(2kT/\pi m) = kT/\pi$. We shall now discuss some of the properties of liquids associated with formulae (6) and (7).

**§ 803. Relationship of liquid to gas and to crystal.** Either of the models discussed in the preceding section, though crude, is adequate to clarify the relationship of a liquid on the one hand to a gas, and on the other to a crystal. The relationship to a gas is most clearly seen from the uniform potential model. As the dilution increases, $\chi(V)$ decreases and $v(V)$ increases. In the limit of increasing $V$ we have $\chi(V) \to 0$ and $v(V) \to V$ so that formula (802, 6) becomes identical with that for a perfect gas This shows clearly the continuity between the liquid and the gaseous states.

The comparison between the liquid and crystalline states is clearest when we use the harmonic oscillator formula (802, 7). For the free energy $F$ of a crystal made up of $N$ molecules we have, according to (408, 5) and (408, 6),

$$\frac{F}{N} = -\chi_0 + kT\int_0^\infty \log(1-e^{-h\nu/kT})\, g(\nu)\, d\nu - kT\log j(T); \tag{803, 1}$$

we repeat here that in this formula $g(\nu)$ is a distribution function for the acoustical spectrum, such that the number of normal modes with frequencies in the range $\nu$, $\nu+d\nu$ is $Ng(\nu)\,d\nu$, with

$$\int_0^\infty g(\nu)\, d\nu = 3. \tag{803, 2}$$

To obtain an instructive comparison between the liquid and the crystal, it is expedient to use for the crystal a model which is as crude as that used for the liquid. We therefore use Einstein's approximation for $g(\nu)$, according to which all the normal modes have the same frequency $\nu$. This implies

that each molecule in the crystal vibrates about its equilibrium position independently of the remaining molecules, and is just the same approximation as we have made in the harmonic oscillator model of the liquid. To this approximation (1) reduces to

$$\frac{F}{N} = -\chi_0 + 3kT\log(1-e^{-h\nu/kT}) - kT\log j(T). \qquad (803,3)$$

For sufficiently high temperatures, $kT \gg h\nu$, the vibrations will be effectively classical, and (3) takes the limiting form

$$\frac{F}{N} = -\chi_0 - 3kT\log\frac{kT}{h\nu} - kT\log j(T). \qquad (803,4)$$

When we compare this formula with the strictly analogous formula (802, 7) for the liquid, we notice that, apart from $\chi_0$ and $\nu$ having different values for the liquid and the crystal, there is a difference of an extra term $-kT$ in the free energy of the liquid. The corresponding extra term in the molecular entropy is just $k$. This means that for given $\chi_0$ and $\nu$ the liquid is more disordered than the crystal, and this is physically correct. This discontinuity between the thermodynamic functions of liquids and crystals has been especially emphasized by Eyring.* The same discontinuity appears if we use the smoothed potential model instead of that of the harmonic oscillator. To show this let us now treat the whole liquid as a single system. Then the partition function for the whole liquid will be of the form $\{f(T)\}^N/N!$, where $f(T)$ denotes the partition function of a single molecule, and the division by $N!$ is required to eliminate repetitions of physically indistinguishable states. But each molecule can move anywhere in the liquid as long as it does not overlap another molecule and so has an effective free volume $(V-Nb)$ or $Nv$. Thus the partition function of the whole liquid will contain the factor $(Nv)^N/N!$ or $(ev)^N$. In the crystal on the other hand each molecule has its own equilibrium position, and the molecules are localized systems. Consequently the partition function of the whole crystal is simply $\{f(T)\}^N$, where $f(T)$, the partition function for the single molecule, now contains only a volume factor $v$, because the molecule is constrained to remain in the neighbourhood of a single fixed equilibrium position. Thus the partition function of the whole crystal contains the factor $v^N$, where that of the liquid had the factor $(ev)^N$. This leads to an excess molecular entropy in the liquid of $k\log e = k$, in agreement with the value found above.†

* See for example, Hirschfelder, Stevenson and Eyring, *J. Chem. Phys.* **5**, 897 (1937). Cf. Lennard-Jones and Devonshire, *Proc. Roy. Soc.* A, **163**, 61 (1937).

† Earlier formulations of the free energy of a liquid, such as Guggenheim, *Proc. Roy. Soc.* A, **135**, 181 (1932); Mott, *Proc. Roy. Soc.* A, **146**, 465 (1934) and *S.M.* p. 524, omitted the term $-kT$ occurring in (802, 6). These can be made formally correct by assigning to $v$ the value which the present formulation assigns to $ev$, but $v$ would then no longer change continuously into $V$ in the limit of high dilution to the perfect gaseous state.

**§ 804. Derived thermodynamic functions for crude models.** From the alternative formulae (802, 6) and (802, 7) for the free energy we can derive all the other thermodynamic functions for the liquid according to the assumed models. Let us first use the smoothed potential model. For the pressure $P$ we obtain

$$P = -\left(\frac{\partial F}{\partial V}\right)_{T,N} = -\frac{1}{N}\left(\frac{\partial F}{\partial V}\right)_{T,N} = \frac{\partial \chi}{\partial V} + kT\frac{\partial \log v}{\partial V}. \qquad (804, 1)$$

This is formally correct but cannot be applied quantitatively in the absence of knowledge of the dependence of $\chi$ and $v$ on $V$. For ordinary pressures, and temperatures well below the critical temperature, the properties of the liquid such as its volume are insensitive to pressure changes, and for most purposes it is adequate to consider the pressure to be zero. We then have $\partial\chi/\partial V$ and $\partial v/\partial V$ related by

$$\frac{\partial \chi}{\partial V} + kT\frac{\partial \log v}{\partial V} \simeq 0. \qquad (804, 2)$$

The molecular free energy $F$ is given by

$$F = \frac{F}{N} = -\chi - kT\log\frac{(2\pi mkT)^{\frac{3}{2}}\,v(V)}{h^3} - kT - kT\log j(T), \qquad (804, 3)$$

and the partial potential $\mu$ by

$$\mu = F + PV = -\chi - kT\log\frac{(2\pi mkT)^{\frac{3}{2}}\,v(V)}{h^3} - kT - kT\log j(T) + PV. \qquad (804, 4)$$

The molecular energy $E$ is given by

$$E = -T^2\left(\frac{\partial F/T}{\partial T}\right)_{V,N} = -\chi + \tfrac{3}{2}kT + E^{\text{int}}, \qquad (804, 5)$$

where $E^{\text{int}}$ denotes the contributions of the internal molecular degrees of freedom. The molecular heat content $H$ is given by

$$H = E + PV = -\chi + \tfrac{3}{2}kT + E^{\text{int}} + PV. \qquad (804, 6)$$

The analogous formulae for the harmonic oscillator model are

$$P = \frac{\partial \chi_0}{\partial V} - 3kT\frac{\partial \log \nu}{\partial V} \simeq 0, \qquad (804, 7)$$

$$F = -\chi_0 - 3kT\log\frac{kT}{h\nu} - kT - kT\log j(T), \qquad (804, 8)$$

$$\mu = -\chi_0 - 3kT\log\frac{kT}{h\nu} - kT - kT\log j(T) + PV, \qquad (804, 9)$$

$$E = -\chi_0 + 3kT + E^{\text{int}}, \qquad (804, 10)$$

$$H = -\chi_0 + 3kT + E^{\text{int}} + PV. \qquad (804, 11)$$

For ordinary pressures the $PV$ term is negligible in all these formulae.

Since both the models for which we have derived formulae are rather crude, we cannot expect them to lead to results of high accuracy. For semi-quantitative comparison with experiment both are useful, and we may in any particular application use whichever is the more convenient. Usually it is convenient to use the smoothed potential model for correlating the properties of a liquid with those of a gas, and the harmonic oscillator model for correlating the properties of a liquid with those of a crystal.

**§ 805. Elementary thermodynamic theory of melting.** The partial potential of a liquid at ordinary pressures, if we use the harmonic oscillator model, is according to (804, 9)

$$\mu^L = -\chi_0^L - 3kT\log\frac{kT}{h\nu^L} - kT - kT\log j^L(T) + PV^L, \qquad (805, 1)$$

where we use the superscript $L$ to specify the liquid phase. The analogous formula for the crystal, according to Einstein's approximation, is

$$\mu^K = -\chi_0^K - 3kT\log\frac{kT}{h\nu^K} - kT\log j^K(T) + PV^K, \qquad (805, 2)$$

where the superscript $K$ denotes the crystal phase. We may assume that in the regularly ordered configuration of the solid crystal the assembly contains less potential energy than in the irregular configurations of the liquid, and owing to its regularity and rigidity a natural frequency $\nu^K$ which is greater than $\nu^L$. Since then $\chi_0^L < \chi_0^K$ and $\nu^L < \nu^K$, we have $\mu^K < \mu^L$ for small $T$ but for sufficiently large $T$ we have $\mu^L > \mu^K$. At some temperature, we shall have $\mu^L = \mu^K$ and this fixes the melting-point. If we assume that there is no discontinuity between the internal degrees of freedom in the liquid and the crystal at the melting-point, so that $j^L(T) = j^K(T)$, then the temperature $T_m$ of melting is given by

$$\frac{\chi_0^K - \chi_0^L}{kT_m} = 3\log\frac{\nu^K}{\nu^L} + 1. \qquad (805, 3)$$

We ignore the small term $P(V^L - V^K)/kT_m$. Using formula (804, 1) for the molecular heat content in the liquid, and an exactly analogous formula for that in the crystal, and assuming no discontinuity in the internal molecular degrees of freedom, we obtain for $\Lambda_m$ the molecular heat of melting

$$\Lambda_m = H^L - H^K = \chi_0^K - \chi_0^L. \qquad (805, 4)$$

Substituting (4) into (3), we obtain for $\Lambda_m/T_m$ the entropy of melting

$$\frac{\Lambda_m}{T_m} = 3k\log\frac{\nu^K}{\nu^L} + k. \qquad (805, 5)$$

Since $\nu^K$ will be greater than $\nu^L$, but will usually not differ greatly from $\nu^L$,

we should expect from (5) that the molecular entropy of melting should exceed, but not greatly exceed, $k$. The extent to which this is verified for metals is shown in Table 1. According to the theory the value of $\Lambda_m/kT_m$ should somewhat exceed unity. The experimental values are given in the fourth column of the table. The formulae used depend on the assumption,

TABLE 1

*Heats and entropies of fusion for various metals*

| Metal | $\mathbf{N}\Lambda_m$ (cal./mole) | $T_m$ (° K.) | $\frac{\Lambda_m}{kT_m} = \frac{\mathbf{N}\Lambda_m}{RT_m}$ | $\frac{T_m}{\Theta}$ |
|---|---|---|---|---|
| Li | 830 | 459 | 0·90 | 0·9 |
| Na | 630 | 370 | 0·85 | 1·85 |
| K | 570 | 335 | 0·85 | 2·65 |
| Rb | 520 | 311 | 0·85 | 3·65 |
| Cs | 500 | 299 | 1·7 | 4·4 |
| Cu | 2750 | 1356 | 1·0 | 8·9 |
| Ag | 2630 | 1233 | 1·1 | 5·7 |
| Au | 3180 | 1336 | 1·2 | 7·7 |
| Zn | 1700 | 692 | 1·2 | 2·9 |
| Cd | 1500 | 594 | 1·25 | 3·5 |
| Hg | 560 | 234 | 1·2 | 2·4 |
| Al | 1910 | 933 | 1·0 | 2·3 |
| Ga | 1320 | 303 | 2·2 | — |
| Tl | 1470 | 580 | 1·3 | 6·0 |
| Pb | 1120 | 590 | 0·95 | 6·6 |
| Sb | 4660 | 903 | 2·6 | — |
| Bi | 2600 | 544 | 2·4 | -- |

amongst others, that the vibrations are effectively classical, that is to say that the temperature $T_m$ of melting should be large compared with the characteristic temperature $\Theta = h\nu/k$. The values of the ratio $T_m/\Theta$ for the crystal phases are given, when known, in the last column. It will be seen that, excluding Li and Na, for which the condition $T_m/\Theta \gg 1$ is hardly satisfied, and the semi-metallic Sb, Bi, which may well have a quite different molecular or electronic structure in the solid and liquid phases, eight out of thirteen metals have $\Lambda_m/kT_m$ between 1 and 1·3 while twelve out of thirteen have $\Lambda_m/kT_m$ between 0·85 and 2·0. This agreement may be regarded as satisfactory for such a crude theory. It has been pointed out by Mott and Gurney† that it is only a rough approximation to retain the extra factor $e$

* An attempt has been made by Hirschfelder, Stevenson and Eyring to account accurately for the values of entropies of fusion. They give a clear and instructive qualitative discussion of the process of melting, *J. Chem. Phys.* 5, 898 (1937). We, however, do not refer to their computations because these are largely dependent on an entirely empirical equation of state.

† Mott and Gurney, *Trans. Fara. Soc.* **35**, 364 (1939). See also a very recent article, Mott and Gurney, *Phys. Soc. Rep. Prog. Phys.* **5**, 46 (1939), which gives an excellent review of the theories of liquids including the ground covered in §§ 802–806.

in $\{\Omega(T)\}^{1/N}$ as we have done here following Eyring. The true factor is not a constant, but falls below the value $e$ as the temperature of the liquid falls, and near the freezing-point, which is the temperature we are concerned with in this comparison, this factor may fall to a value much more nearly unity than $e$. The term $k$ in (5) will then fall to a small fraction of $k$, and the term depending on $\nu^K/\nu^L$ may become dominant. Mott* has made an interesting study of formula (5) with the term $k$ omitted near the freezing-point for metals, by correlating $\nu^K/\nu^L$ with the change in electrical conductivity on melting according to the standard theory of electronic conduction in metals. This correlation enables $\nu^K/\nu^L$ to be derived from observed conductivities so that $\Lambda_m$ can be calculated from the conductivities and compared with the directly observed heat of melting. The comparison is strikingly successful.

**§ 806. Estimations of free volume from thermal expansion and compressibility.** As already mentioned, we can in principle derive all the thermodynamic properties of the liquid from the formulae for the free energy, but many of these formulae would be useless in the absence of knowledge of such quantities as $\partial\chi/\partial V$ and $\partial v/\partial V$ or $\partial\chi_0/\partial V$ and $\partial\nu/\partial V$. We shall therefore endeavour to obtain formulae in which such unknown quantities do not occur. We can in fact obtain formulae of physical interest from which the unknown $\partial\chi/\partial V$ is eliminated, but we shall be obliged to make some assumptions concerning the dependence of $v$ on $V$. In the smoothed potential model the pressure is given by (804, 1). If we now differentiate this with respect to $T$ keeping $N$, $V$ constant and remembering that $\chi$, $v$ are by hypothesis functions of $V$ only, we obtain

$$\left(\frac{\partial P}{\partial T}\right)_{V,N} = k\frac{\partial \log v}{\partial V}. \tag{806, 1}$$

But if $\alpha$ denotes the coefficient of thermal expansion and $\beta$ the compressibility, we have

$$\frac{\alpha}{\beta} = -\frac{(\partial V/\partial T)_P}{(\partial V/\partial P)_T} = \left(\frac{\partial P}{\partial T}\right)_V = \left(\frac{\partial P}{\partial T}\right)_{V,N}. \tag{806, 2}$$

Thus by substitution from (2) into (1)

$$\frac{\alpha}{\beta} = k\frac{\partial \log v}{\partial V}. \tag{806, 3}$$

The simplest possible assumption concerning $v$ resembles that made by van der Waals, namely

$$v = V - V_0, \tag{806, 4}$$

where $V_0$ is a constant for the liquid, not necessarily equal to the similar constant $b$ for the slightly imperfect gas. If we assume the validity of (4)

* Mott, *Proc. Roy. Soc.* A, **146**, 465 (1934).

and substitute into (3), we obtain

$$\alpha/\beta = k/v. \tag{806, 5}$$

For a large number, if not the majority, of liquids with non-polar molecules $\alpha \simeq 1 \times 10^{-3}$ deg.$^{-1}$ and $\beta \simeq 1 \times 10^{-4}$ atm.$^{-1}$. Using these values, together with $R = \mathbf{N}k = 82$ atm. cm.$^3$/deg. mole, we obtain for the molar free volume $\mathbf{N}v = R\beta/\alpha \simeq 8$ cm.$^3$/mole. We shall shortly obtain an independent estimate of $v$ from the vapour pressures of liquids. We shall first consider an alternative form for the dependence of $v$ on $V$.

Instead of using van der Waals' form for $v$, we might suppose each molecule free to move in a spherical cage, whose radius is equal to the average distance $a$ between the centres of two molecules which are nearest neighbours, diminished by the diameter $D$ of a molecule regarded as a rigid sphere. This assumption can be expressed by*

$$v = \tfrac{4}{3}\pi(a-D)^3. \tag{806, 6}$$

Now the molecular volume $V$ is related to $a$ by

$$a^3 = \gamma V, \tag{806, 7}$$

where $\gamma$ is a numerical constant of the order of magnitude unity, determined by the geometry of the packing. If the molecules are arranged as in a face-centred cubic crystal, it can be shown that $\gamma = \sqrt{2}$. We can combine (6) and (7) to give

$$v = \gamma\tfrac{4}{3}\pi(V^{\frac{1}{3}} - V_0^{\frac{1}{3}})^3, \tag{806, 8}$$

where $V_0$ is a new constant defined by $\gamma V_0 = D^3$. From (8) we deduce

$$\frac{\partial \log v}{\partial V} = \frac{1}{V^{\frac{2}{3}}(V^{\frac{1}{3}} - V_0^{\frac{1}{3}})} = \frac{(\gamma\frac{4}{3}\pi)^{\frac{1}{3}}}{V^{\frac{2}{3}}v^{\frac{1}{3}}}. \tag{806, 9}$$

Substituting (9) into (3), we obtain

$$\frac{\alpha}{\beta} = \frac{k(\gamma\frac{4}{3}\pi)^{\frac{1}{3}}}{V^{\frac{2}{3}}v^{\frac{1}{3}}}. \tag{806, 10}$$

Assuming the same approximate values for $\alpha$ and $\beta$ as before, we obtain $\mathbf{N}(\gamma\frac{4}{3}\pi)^{-\frac{1}{3}} V^{\frac{2}{3}} v^{\frac{1}{3}} \sim 8$ cm.$^3$/mole. If we set $\gamma = \sqrt{2}$, corresponding to face-centred cubic packing, this gives $\mathbf{N}V^{\frac{2}{3}}v^{\frac{1}{3}} \sim 14$ cm.$^3$/mole. Taking chloroform at ordinary temperatures as a typical example we have $\mathbf{N}V = 80$ cm.$^3$/mole, so that $\mathbf{N}v \sim 0{\cdot}44$ cm.$^3$/mole, as compared with the value 8 cm.$^3$ obtained from (4).

**§ 807. Estimate of free volume from the vapour pressure. Trouton's rule.** We shall now obtain an independent estimate of $v$ from the vapour pressure of a liquid. The equilibrium condition between vapour and liquid is as usual

$$\mu^G = \mu^L, \tag{807, 1}$$

* This formula for the free volume is used by Lennard-Jones and Devonshire, *Proc. Roy. Soc.* A. **163**, 59 (1937), and is a modification of a similar formula used by Eyring and Hirschfelder, *J. Phys. Chem.* **41**, 250 (1937).

where the superscripts $G$, $L$ refer to the gaseous and liquid phases respectively. For $\mu^G$ we have according to § 510

$$\mu^G = kT\log p - kT\log\frac{(2\pi m)^{\frac{3}{2}}(kT)^{\frac{5}{2}}}{h^3} - kT\log j^G(T), \qquad (807, 2)$$

while $\mu^L$ is given by (804, 4). Substituting from (2) and (804, 4) into (1) and assuming the partition functions $j(T)$ for the internal degrees of freedom to be equal in the two phases, we obtain

$$\log p = -\frac{\chi}{kT} + \log\frac{kT}{ev} + \frac{PV^L}{kT}, \qquad (807, 3)$$

or

$$p = \frac{kT}{v} e^{-(\chi+kT)/kT} e^{PV^L/kT}. \qquad (807, 4)$$

The molecular heat content in the liquid is according to (804, 6)

$$H^L = -\chi + \tfrac{3}{2}kT + E^{\text{int}} + PV^L, \qquad (807, 5)$$

whereas that in the gas is given by

$$H^G = -T^2\left(\frac{\partial \mu^G/T}{\partial T}\right)_p = \tfrac{5}{2}kT + E^{\text{int}}, \qquad (807, 6)$$

if we assume the internal molecular contributions $E^{\text{int}}$ to be equal in the two phases. For the molecular heat of evaporation $\Lambda_e$ we thus obtain

$$\Lambda_e = H^G - H^L = \chi + kT - PV^L. \qquad (807, 7)$$

Using (7) we can rewrite (4) as

$$p = \frac{kT}{v} e^{-\Lambda_e/kT}. \qquad (807, 8)$$

At all ordinary pressures $PV^L$ is negligibly small compared with $kT$, and might without loss of accuracy be omitted whenever it occurs. Its omission sometimes, however, leads to apparent inconsistencies on differentiation, and it is therefore safer to include these terms, even though small, until the final stage.

We can alternatively derive (7) by applying thermodynamics directly to (3) but great caution is required. We obtain

$$\Lambda_e = kT^2\left(\frac{\partial \log p}{\partial T}\right)_P = kT^2\left(\frac{\partial \log p}{\partial T}\right)_{P,V^L} + kT^2\left(\frac{\partial \log p}{\partial V^L}\right)_{T,P}\left(\frac{\partial V^L}{\partial T}\right)_P. \qquad (807, 9)$$

Since $\chi$ and $v$ are assumed to be functions of $V$, we obtain from (3)

$$kT\left(\frac{\partial \log p}{\partial V^L}\right)_T = -\frac{\partial \chi}{\partial V^L} - kT\frac{\partial \log v}{\partial V^L} + P = 0, \qquad (807, 10)$$

by (804, 1). Hence (9) reduces to the much simpler formula

$$\Lambda_e = kT^2\left(\frac{\partial \log p}{\partial T}\right)_{P,V^L}. \qquad (807, 11)$$

Substitution of (3) into (11) leads directly to (7).

TABLE 2

*Heats and entropies of evaporation at the boiling-point for various liquids*

| Substance | $T_b$ (°K.) | $\mathbf{N}\Lambda_e$ (K.cal./mole) | $\mathbf{N}\Lambda_e/T_b$ (cal./deg. mole) |
|---|---|---|---|
| Neon | 27·2 | 0·415 | 15·3 |
| Nitrogen | 77·5 | 1·36 | 17·6 |
| Argon | 87·5 | 1·50 | 17·2 |
| Oxygen | 90·6 | 1·66 | 18·3 |
| Ethyl ether | 307 | 6·47 | 21·1 |
| Carbon disulphide | 319 | 6·49 | 20·4 |
| Chloroform | 334 | 6·97 | 20·8 |
| Carbon tetrachloride | 350 | 7·14 | 20·4 |
| Benzene | 353 | 7·35 | 20·8 |
| Methyl salicylate | 497 | 11·00 | 22·2 |
| Organic compounds (non associated) | — | | 20 to 23 |
| Helium | 4·29 | 0·022 | 5·1 |
| Hydrogen | 20·4 | 0·214 | 10·5 |
| Methyl alcohol | 337·7 | 8·38 | 24·8 |
| Formic acid | 373·6 | 5·54 | 14·8 |

The vapour pressures of almost all liquids can be expressed with high accuracy over a wide temperature range, which includes the boiling-point, by an empirical formula of the form

$$p = ae^{-\Lambda_e/kT}, \qquad (807, 12)$$

where $a$ is nearly constant.* Moreover for a large number of substances with non-polar molecules the value of $a$ does not differ greatly from one liquid to another. Using an average value of $a$ for such liquids, we have empirically

$$p \simeq 2 \times 10^7 e^{-\Lambda_e/kT}\,\text{mm. Hg} \simeq 2\cdot7 \times 10^4 e^{-\Lambda_e/kT}\,\text{atm.} \qquad (807, 13)$$

This formula is usually correct to within a factor varying between $\frac{1}{2}$ and 2. The boiling-point $T_b$ of a liquid at atmospheric pressure according to (13) satisfies the relation

$$\frac{\Lambda_e}{kT_b} = \log_e(2\cdot7 \times 10^4) = 10. \qquad (807, 14)$$

This can also be expressed as $\mathbf{N}\Lambda_e/T_b = 10\mathbf{N}k = 10R = 20$ cal./deg. mole.

* If $a$ were strictly constant, comparison of (8) and (12) would lead to $v \propto T$. This relation combined with (806, 8) would enable one to calculate the temperature dependence of the coefficient of thermal expansion. It seems, however, unlikely that the constancy of $a$ is sufficiently exact to warrant such a procedure.

This empirical relation is known as Trouton's rule and its degree of accuracy is shown by the data in Table 2. We must exclude hydrogen and helium, because such light molecules may not be treated classically, and compounds containing hydroxyl or amino groups owing to the probability of some form of association. Moreover Trouton's rule can be expected to apply only to normal liquids. Even for normal liquids, however, the deviations from Trouton's rule are definite and systematic. This is clearly

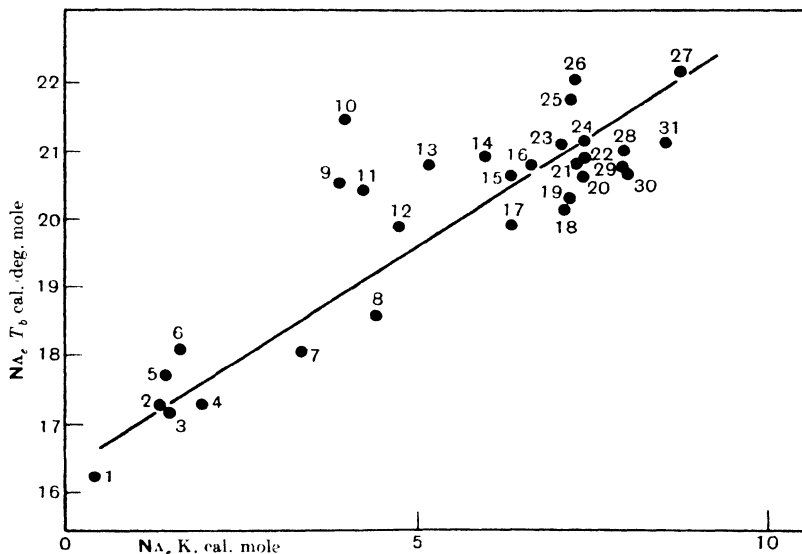



Fig. 1. Trouton's ratio at the boiling-point.

1. Neon.
2. Nitrogen.
3. Argon.
4. Methane.
5. Carbon monoxide.
6. Oxygen.
7. Ethane.
8. Chlorine.
9. Hydrochloric acid.
10. Nitrous oxide.
11. Hydrobromic acid.
12. Hydriodic acid.
13. Methyl chloride.
14. Ethyl chloride.
15. *iso*-Propyl chloride.
16. *n*-Propyl chloride.
17. Carbon disulphide.
18. Acetonitrile.
19. Hexane.
20. *t*-Amyl chloride.
21. Carbon tetrachloride.
22. Benzene.
23. Chloroform.
24. *n*-Butyl chloride.
25. Silicon tetrachloride.
26. Acetone.
27. *iso*-Amyl bromide.
28. *n*-Amyl chloride.
29. Toluene.
30. Stannic chloride.
31. Chlorobenzene.

shown in Fig. 1, which is due to Barclay and Butler.* It is clear from this figure that for normal liquids $\Lambda_e/T_b$ by no means has a universal value, but rather varies linearly with $\Lambda_e$. No convincing theoretical explanation of this improved empirical rule has yet been given. In spite of these systematic deviations, Trouton's rule is a useful rough approximation.

* Barclay and Butler, *Trans. Fara. Soc.* **34**, 1445 (1938).

If now we compare at the boiling-point Trouton's rule as expressed by the empirical formula (13) with the theoretical formula (8), we obtain

$$\mathbf{N}v = \frac{\mathbf{N}kT_b}{2\cdot 7\times 10^4\,\text{atm.}} = \frac{RT_b}{2\cdot 7\times 10^4\,\text{atm.}}. \qquad (807,\,15)$$

To obtain the order of magnitude of $v$ let us set $T_b = 334$, the boiling-point of chloroform. At this temperature $RT_b = 2\cdot 7\times 10^4$ atm. cm.$^3$/mole. Inserting this value into (15), we obtain $\mathbf{N}v \sim 1$ cm.$^3$. When we compare this value with those calculated from thermal expansion and compressibility, we find reasonable agreement with the value $\mathbf{N}v \sim 0\cdot 44$ cm.$^3$ obtained from (806. 6) but less good agreement with the value 8 cm.$^3$ obtained from (806, 4).

We have given details of the comparison for chloroform only, but most other normal liquids would lead to similar results. We see then that the value that has to be assigned to the free volume $v$ to give the correct vapour pressures agrees reasonably well with the value which fits the thermal expansion and compressibility when formula (806. 6) is used. We conclude that this is a reasonably useful form to assume* for the dependence of the free volume $v$ on the molecular volume $V$.

All the preceding formulae of the present section are based on the smoothed potential model. Analogous formulae corresponding to the harmonic oscillator model are readily obtained by substituting from (802, 8) for $v$. We thus obtain, in particular, as the analogue of (8)

$$p = \frac{(2\pi m)^{\frac{3}{2}}\,\nu^3}{(kT)^{\frac{1}{2}}}\,e^{-\chi_0/kT}. \qquad (807,\,16)$$

A formula equivalent to (16) was obtained by Mie† many years before the use of the smoothed potential model.

**§ 808. Refined model for liquids and compressed gases.** In the two crude models of the liquids so far considered the constants $\chi$, $v$ in the one model, and $\chi_0$, $\nu$ in the other, have been treated as adjustable parameters. Both models are simple cases of a more general model, in which each molecule can move about the available volume in a definite field of force, determined by the interaction energy between the molecule and its neighbours. Recently an important advance has been made by Lennard-Jones and Devonshire,‡ who have used a model of this kind to calculate the equilibrium properties of a liquid or highly compressed gas, assuming for the interaction energy the value already found empirically to fit the properties

* The idea of correlating the free volume with the thermal expansion, compressibility and vapour pressure is due to Eyring and Hirschfelder, *J. Phys. Chem.* **41**, 249 (1937). We have here used a somewhat different method of correlation from theirs.

† Mie, *Ann. d. Phys.* **11**, 657 (1903).

‡ Lennard-Jones and Devonshire, *Proc. Roy. Soc.* A, **163**, 53 (1937); **165**, 1 (1938).

of the slightly imperfect gas. It is satisfactory to find that the interaction energy $\epsilon(r)$ can be chosen so as to give with satisfactory accuracy on the one hand the temperature dependence of the virial coefficient $B$ of the slightly imperfect gas, and on the other the critical temperature, the boiling-point, and heat of evaporation. We shall describe in some detail the procedure adopted by Lennard-Jones and Devonshire.

Instead of assuming the potential energy of a molecule within its available volume either to be constant or to be that corresponding to an isotropic harmonic oscillator, we endeavour to calculate its potential energy due to all its immediate neighbours, as a function of position and also of the size of the available volume. Each molecule is considered to be confined to its own cell from which others are excluded. This approximation is the more reasonable the greater the density. Whereas in a sparse gas binary encounters alone are important, and an atom can migrate rapidly from one part of the assembly to another, in a dense gas or in a liquid an atom will be imprisoned by its immediate neighbours, and will escape from one environment to another the more rarely the greater the density. We continue to neglect these infrequent migrations except in so far as they contribute an extra term $-kT$ to the free energy of a liquid or a dense gas as compared with the free energy of a crystal. The presence of this term has been explained in § 803. As each molecule moves about in its cell, the field in which it moves will be that due to all the other molecules and will vary with the time. We need to replace this fluctuating field by a suitable average. The simplest assumption we can make is that the average field in which any one molecule moves is that due to its immediate neighbours when each is in its equilibrium position, that is, at the centre of its own cell; we shall consider this case as a suitable first approximation

Since atomic fields fall off very rapidly with distance, we shall consider only nearest neighbours. The problem we have to deal with, therefore, is that of a particle moving in the field of a number of other particles symmetrically arranged on the surface of a sphere. If the immediate neighbours (generally about twelve) are fairly closely packed, the field within the cell will have a high degree of symmetry, and it will be sufficient for our purpose to replace the actual field by one which is spherically symmetrical about the centre of the cell This may be obtained by taking a suitable average. We may take the average field as the molecule within the cell describes a sphere about the centre. This is equivalent to the average potential produced within the cell, when the nearest neighbours take up all positions with equal probability on the surface of a sphere.

Let $a$ be the average distance between nearest neighbours, and let $\epsilon(a)$ be their mutual potential energy at this distance apart. We suppose one

molecule kept fixed while the other is moved about a sphere of radius $r$, whose centre is at a distance $a$ from the fixed molecule. The average mutual potential energy $\bar{\epsilon}(r)$ of the two particles may then be shown to be

$$\bar{\epsilon}(r) = \tfrac{1}{2}\int_0^\pi \epsilon\{(r^2+a^2-2ar\cos\theta)^{\frac{1}{2}}\}\sin\theta\,d\theta. \qquad (808,1)$$

If $z$ is the number of nearest neighbours of a given molecule, its average potential energy $w(r)$ within a cell for $r<a$ may be written as

$$w(r) = z\bar{\epsilon}(r) = \tfrac{1}{2}z\int_0^\pi \epsilon\{(r^2+a^2-2ar\cos\theta)^{\frac{1}{2}}\}\sin\theta\,d\theta. \qquad (808,2)$$

In order to make further progress it is necessary to assume a definite form for $\epsilon(r)$. We saw in Chapter VII that the equilibrium properties of slightly imperfect gases could be accurately interpreted by assuming an energy of interaction between pairs of molecules of the form

$$\epsilon(r) = -\frac{\mu}{r^6}+\frac{\nu}{r^n}, \qquad (808,3)$$

where $n$ can be given any value between 9 and 14, provided that suitable values are assigned to the constants $\mu$ and $\nu$. Theoretically there is nothing to choose between the alternative values of $n$ and for arithmetical convenience we choose $n = 12$. We thus assume

$$\epsilon(r) = -\frac{\mu}{r^6}+\frac{\nu}{r^{12}} = -2|\epsilon^*|\left(\frac{r^*}{r}\right)^6+|\epsilon^*|\left(\frac{r^*}{r}\right)^{12}, \qquad (808,4)$$

where $\epsilon^*$ denotes the minimum value of $\epsilon$, and $r^*$ is the value of $r$ at which this minimum occurs. The parameters $\epsilon^*$, $r^*$ are related to the parameters $\mu$, $\nu$ by

$$\epsilon^* = -|\epsilon^*| = -\mu^2/4\nu, \qquad (808,5)$$

$$r^* = (2\nu/\mu)^{\frac{1}{6}}. \qquad (808,6)$$

When we substitute (4) into (2), we obtain

$$w(r) = \tfrac{1}{2}z|\epsilon^*|\int_0^\pi \left\{-\frac{2r^{*6}}{(r^2+a^2-2ar\cos\theta)^3}+\frac{r^{*12}}{(r^2+a^2-2ar\cos\theta)^6}\right\}\sin\theta\,d\theta$$

$$= \tfrac{1}{2}z|\epsilon^*|\left[-\frac{r^{*6}}{2a^5r}\left\{\left(1-\frac{r}{a}\right)^{-4}-\left(1+\frac{r}{a}\right)^{-4}\right\}+\frac{r^{*12}}{10a^{11}r}\left\{\left(1-\frac{r}{a}\right)^{-10}-\left(1+\frac{r}{a}\right)^{-10}\right\}\right]. \qquad (808,7)$$

In the limit $r\to 0$ this becomes

$$w(0) = \tfrac{1}{2}z|\epsilon^*|\left[-4\left(\frac{r^*}{a}\right)^6+2\left(\frac{r^*}{a}\right)^{12}\right]. \qquad (808,8)$$

Using (8) we can rewrite (7) in the form

$$w(r)-w(0) = z|\epsilon^*|\left\{\left(\frac{r^*}{a}\right)^{12}l\left(\frac{r^2}{a^2}\right)-2\left(\frac{r^*}{a}\right)^6 m\left(\frac{r^2}{a^2}\right)\right\}, \qquad (808,9)$$

where $l(y)$, $m(y)$ are functions defined by

$$l(y) = (1+12y+25{\cdot}2y^2+12y^3+y^4)(1-y)^{-10}-1, \qquad (808,10)$$

$$m(y) = (1+y)(1-y)^{-4}-1. \qquad (808,11)$$

It is convenient to introduce a positive energy $\Lambda^*$ defined by

$$\Lambda^* = -z\epsilon^* \qquad (808,12)$$

according to (5), and a volume $V^*$ defined by

$$V^* = \frac{V}{a^3}r^{*3} = \frac{r^{*3}}{\gamma}, \qquad (808,13)$$

where $V$, as usual, denotes the volume per molecule, and $\gamma$, defined by

$$a^3 = \gamma V, \qquad (808,14)$$

is a numerical constant determined by the geometrical arrangement of the molecules. For a face-centred cubic lattice $\gamma = \sqrt{2}$. Introducing the new constants $\Lambda^*$ and $V^*$, we can rewrite (9) as

$$w(r)-w(0) = \Lambda^*\left\{\left(\frac{V^*}{V}\right)^4 l\left(\frac{r^2}{a^2}\right) - 2\left(\frac{V^*}{V}\right)^2 m\left(\frac{r^2}{a^2}\right)\right\}. \qquad (808,15)$$

We can also rewrite (8) as

$$w(0) = \Lambda^*\left\{-2\left(\frac{V^*}{V}\right)^2 + \left(\frac{V^*}{V}\right)^4\right\}. \qquad (808,16)$$

Formula (15) tells us how the potential energy of a given molecule varies as it moves in its cell, while (16) gives the value of this potential at the centre of the cell. The zero of energy is, as usual, that of infinite separation. The right-hand side of (16) is a function of $\Lambda^*$ and $V^*/V$ only; that of (15) depends on these two quantities and also, through $a$, on the geometrical constant $\gamma$.

Some representative curves for $w(r)$ for certain values of $V^*/V$ are shown in Fig. 2. Curves $(a_1)$ and $(a_2)$ have a potential hump at the centre, while $(b)$ has not. It is found that the field ceases to have this central hump when $V/V^*$ is approximately 1·6. It will appear later that at the critical point $V = V_c \simeq 2V^*$; the height of the hump is then approximately $\frac{1}{2}kT_c$, where $T_c$ denotes the critical temperature. For $V/V^* = 3{\cdot}16$ the height is $0{\cdot}9kT_c$. The general shapes of these curves show why the model in which each molecule wanders around the centre of its cell is satisfactory as long as $V$ is less than about $2V^*$. They also show why the approximations used become less justifiable for larger molecular volumes, that is for more dilute gases.

For the partition function for the motion of each molecule in a given cell, referred to an energy zero with the particle at the centre of the cell,

we have, using (15),

$$\frac{(2\pi m kT)^{\frac{3}{2}}}{h^3}\int_0^{\frac{1}{2}a} 4\pi r^2\, e^{\{u(r)-u(0)\}/kT}dr$$

$$=\frac{(2\pi m kT)^{\frac{3}{2}}}{h^3}\,2\pi a^3\int_0^{\frac{1}{4}} y^{\frac{1}{2}}\exp\left[\frac{\Lambda^*}{kT}\left\{-\left(\frac{V^*}{V}\right)^4 l(y)+2\left(\frac{V^*}{V}\right)^2 m(y)\right\}\right]dy.$$

(808, 17)

The choice of the upper limit for the integral appears to be arbitrary, but Lennard-Jones and Devonshire consider that the choice is unimportant

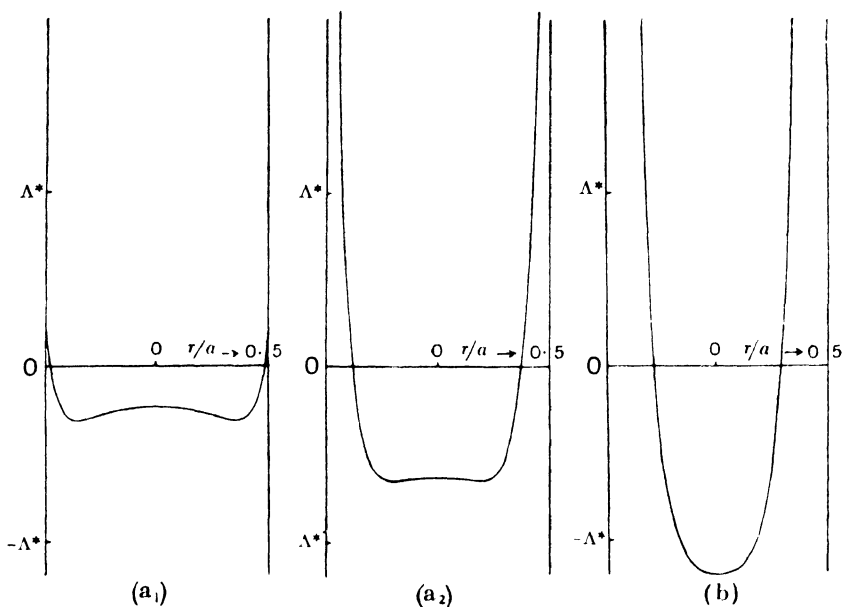



Fig. 2. The potential field within a cell; curves $(a_1)$, $(a_2)$ and $(b)$ correspond to $V/V^* = 3{\cdot}16$, $1{\cdot}83$ and $1{\cdot}20$ respectively.

since most of the contribution to the integral must presumably come from values of $r$ small compared with $\frac{1}{2}a$.

If we denote by $-N\chi_0$ the energy of the assembly when each molecule is at the centre of its cell, referred to an energy zero at infinite separation of the molecules, then referred to this zero the partition function for the motion of each molecule in a given cell becomes

$$\frac{(2\pi m kT)^{\frac{3}{2}}}{h^3}\,e^{\chi_0/kT}\,2\pi a^3\int_0^{\frac{1}{4}} y^{\frac{1}{2}}\exp\left[\frac{\Lambda^*}{kT}\left\{-\left(\frac{V^*}{V}\right)^4 l(y)+2\left(\frac{V^*}{V}\right)^2 m(y)\right\}\right]dy.$$

(808, 18)

But since all the $N$ cells are available for each molecule, the complete partition function for the motion of each molecule through the assembly is

$$\frac{(2\pi mkT)^{\frac{3}{2}}}{h^3} e^{\chi_0/kT}\, 2\pi Na^3 \int_0^{\frac{1}{2}} y^{\frac{1}{2}} \exp\left[\frac{\Lambda^*}{kT}\left\{-\left(\frac{V^*}{V}\right)^4 l(y) + 2\left(\frac{V^*}{V}\right)^2 m(y)\right\}\right] dy. \tag{808, 19}$$

We obtain $\Omega(T)$ from this by omitting the kinetic factor $(2\pi mkT)^{\frac{3}{2}}/h^3$, raising the remaining factor to the power of $N$, and dividing by $N!$. We obtain

$$\log\Omega(T) = N + N\chi_0/kT + N\log(2\pi a^3) + N\log\left[\int_0^{\frac{1}{2}} y^{\frac{1}{2}} \exp\left\{-\frac{\Lambda^*}{kT}\left(\frac{V^*}{V}\right)^4 l(y) + 2\frac{\Lambda^*}{kT}\left(\frac{V^*}{V}\right)^2 m(y)\right\} dy\right]. \tag{808, 20}$$

When we substitute from (20) into (801, 1), we obtain

$$F = \frac{F}{N} = -kT\log\frac{(2\pi mkT)^{\frac{3}{2}}}{h^3} - kT\log j(T) - kT - \chi_0 - kT\log\left[2\pi a^3\int_0^{\frac{1}{2}} y^{\frac{1}{2}} \exp\left\{-\frac{\Lambda^*}{kT}\left(\frac{V^*}{V}\right)^4 l(y) + 2\frac{\Lambda^*}{kT}\left(\frac{V^*}{V}\right)^2 m(y)\right\} dy\right]. \tag{808, 21}$$

The energy $\chi_0$ is evidently closely related to $w(0)$, and at least approximately

$$-\chi_0 = \tfrac{1}{2}w(0) = \Lambda^*\{-(V^*/V)^2 + \tfrac{1}{2}(V^*/V)^4\}, \tag{808, 22}$$

the factor $\frac{1}{2}$ being required so as not to count the interaction energy between each pair of neighbours twice over. In formula (22) all energies of interaction are ignored except those between nearest neighbours. This formula can be improved by including an extra term to take account of the interactions of molecules which are not nearest neighbours. It has been shown† that for a face-centred cubic structure the interaction between such molecules increases the attractive term by about 20 % and has a negligible effect on the repulsive term. We have therefore instead of (22)

$$-\chi_0 = \Lambda^*\{-1{\cdot}2(V^*/V)^2 + 0{\cdot}5(V^*/V)^4\}. \tag{808, 23}$$

When we substitute this value of $\chi_0$ into (21) we obtain finally for the free energy

$$F = \frac{F}{N} = -kT\log\frac{(2\pi mkT)^{\frac{3}{2}}}{h^3} - kT\log j(T) - kT - \Lambda^*\left\{1{\cdot}2\left(\frac{V^*}{V}\right)^2 - 0{\cdot}5\left(\frac{V^*}{V}\right)^4\right\} - kT\log(2\pi\gamma gV), \tag{808, 24}$$

† Lennard-Jones and Ingham, *Proc. Roy Soc.* A, **107**, 636 (1925), Table 1.

where $g$ is defined by

$$g = \int_0^{\frac{1}{4}} y^{\frac{1}{2}} \exp\left\{-\frac{\Lambda^*}{kT}\left(\frac{V^*}{V}\right)^4 l(y) + 2\frac{\Lambda^*}{kT}\left(\frac{V^*}{V}\right)^2 m(y)\right\} dy, \quad (808, 25)$$

and is thus a function of $\Lambda^*/kT$ and of $V^*/V$ only, while $\gamma$ is defined by (14).

If we compare formula (24) with formula (802, 6) for the smoothed potential model, we see that they can be made to agree formally by taking $\chi$ as equal to $\chi_0$ given by (23), and by defining the free volume $v$ by

$$v = 2\pi\gamma g V. \quad (808, 26)$$

The agreement is, however, purely formal since $g$ is not a function of $V$ only, but depends also on $T$.

**§ 809. Equation of state and derived thermodynamic functions. Corresponding states.** Having once obtained formula (808, 24) for the free energy, any other thermodynamic properties can be derived by the usual thermodynamic formulae. In particular the pressure $P$ is given by

$$P = -\left(\frac{\partial F}{\partial V}\right)_{T,N} = \frac{kT}{V}\left[1 - \frac{\Lambda^*}{kT}\left\{2\cdot4\left(\frac{V^*}{V}\right)^2 - 2\cdot0\left(\frac{V^*}{V}\right)^4\right\}\right.$$
$$\left. + 4\frac{\Lambda^*}{kT}\left\{\left(\frac{V^*}{V}\right)^4\frac{g_l}{g} - \left(\frac{V^*}{V}\right)^2\frac{g_m}{g}\right\}\right], \quad (809, 1)$$

where $g_l$ and $g_m$, like $g$, are functions of $\Lambda^*/kT$ and $V^*/V$ only, defined by

$$g_l = \int_0^{\frac{1}{4}} y^{\frac{1}{2}} l(y) \exp\left\{-\frac{\Lambda^*}{kT}\left(\frac{V^*}{V}\right)^4 l(y) + 2\frac{\Lambda^*}{kT}\left(\frac{V^*}{V}\right)^2 m(y)\right\} dy, \quad (809, 2)$$

$$g_m = \int_0^{\frac{1}{4}} y^{\frac{1}{2}} m(y) \exp\left\{-\frac{\Lambda^*}{kT}\left(\frac{V^*}{V}\right)^4 l(y) + 2\frac{\Lambda^*}{kT}\left(\frac{V^*}{V}\right)^2 m(y)\right\} dy. \quad (809, 3)$$

The molecular energy is given by

$$E = -T^2\frac{\partial(F/T)}{\partial T} = \tfrac{3}{2}kT - \Lambda^*\left\{1\cdot2\left(\frac{V^*}{V}\right)^2 - 0\cdot5\left(\frac{V^*}{V}\right)^4\right\}$$
$$+ \Lambda^*\left(\frac{V^*}{V}\right)^4\frac{g_l}{g} - 2\Lambda^*\left(\frac{V^*}{V}\right)^2\frac{g_m}{g} + E^{\text{int}}. \quad (809, 4)$$

The partial potential $\mu$ and the molecular heat content $H$ are obtained by substituting from (808, 24), (1) and (4) into the standard formulae

$$\mu = F + PV, \quad (809, 5)$$

$$H = E + PV. \quad (809, 6)$$

The values of $g$, $g_l$, $g_m$ calculated by numerical integration for two values of $\Lambda^*/kT$ and a range of values of $V/V^*$ are given in Table 3. From these

values the isotherms can be constructed according to formula (1). The values thus obtained for $PV/kT$ are given in Table 4 and in Fig. 3. From the shape of curve II it is clear that the isotherm $kT = \Lambda^*/9$ is very close to the critical one.

In assuming a universal value $n = 12$ as well as $m = 6$, we have reduced the number of adjustable parameters in the interaction energy (808, 4) to two, which we may take to be $\epsilon^*$ and $r^*$. For each substance the specific

TABLE 3

*The functions $g$, $g_l$ and $g_m$*

| $V/V^*$ | $(V^*/V)^2$ | $\Lambda^*/kT = 9$ | | | $\Lambda^*/kT = 10$ | | |
|---|---|---|---|---|---|---|---|
| | | $g$ | $g_l$ | $g_m$ | $g$ | $g_l$ | $g_m$ |
| 1·195 | 0·7 | 0·00180 | 0·000910 | 0·000173 | 0·00161 | 0·000747 | 0·000139 |
| 1·291 | 0·6 | 0·00295 | 0·002042 | 0·000372 | 0·00269 | 0·001723 | 0·000316 |
| 1·414 | 0·5 | 0·00515 | 0·00511 | 0·000875 | 0·00478 | 0·00441 | 0·000762 |
| 1·581 | 0·4 | 0·00964 | 0·01462 | 0·00228 | 0·00916 | 0·01315 | 0·00208 |
| 1·826 | 0·3 | 0·01957 | 0·0495 | 0·00670 | 0·01920 | 0·0468 | 0·00643 |
| 2·236 | 0·2 | 0·0437 | 0·2211 | 0·02366 | 0·0445 | 0·2156 | 0·02347 |
| 2·575 | 0·15 | 0·0676 | 0·543 | 0·0482 | 0·0700 | 0·546 | 0·0493 |
| 3·162 | 0·1 | 0·1069 | 1·635 | 0·1084 | 0·1125 | 1·667 | 0·1126 |

TABLE 4

*Calculated isotherms in the critical region*

| $V/V^*$ | $(V^*/V)^2$ | $\Lambda^*/kT = 9$ | | $\Lambda^*/kT = 10$ | |
|---|---|---|---|---|---|
| | | $PV/kT$ | $PV^*/kT$ | $PV/kT$ | $PV^*/kT$ |
| 1·195 | 0·7 | 1·202 | 1·006 | 0·675 | 0·565 |
| 1·291 | 0·6 | 0·765 | 0·593 | 0·218 | 0·169 |
| 1·414 | 0·5 | 0·573 | 0·406 | 0·046 | 0·033 |
| 1·581 | 0·4 | 0·568 | 0·359 | 0·149 | 0·094 |
| 1·826 | 0·3 | 0·644 | 0·353 | 0·348 | 0·191 |
| 2·236 | 0·2 | 0·788 | 0·352 | 0·531 | 0·237 |
| 2·575 | 0·15 | 0·825 | 0·320 | 0·642 | 0·249 |
| 3·162 | 0·1 | 0 877 | 0·277 | 0·721 | 0·224 |

equilibrium properties of the gas or liquid are therefore completely determined by the values of $\epsilon^*$, $r^*$, $z$ and $\gamma$ for the substance. The whole theory is strictly applicable only in so far as the molecules can be treated as spherically symmetrical, and for such molecules the stable form of lattice is the face-centred cubic with $z = 12$ and $\gamma = \sqrt{2}$. If we assume these values of $z$ and $\gamma$, the specific properties of each substance depend only on two parameters $\epsilon^*$, $r^*$, or alternatively on $\Lambda^*$, $V^*$. We can therefore by dimensional

analysis conclude that the equation of state will have the functional form

$$\frac{PV}{kT} = \phi\left(\frac{kT}{\Lambda^*}, \frac{V}{V^*}\right). \tag{809, 7}$$

If this equation is to be accurate for the slightly imperfect gas, for the highly compressed gas, and for the liquid, $\phi$ may well be a complicated function, and we have no reason to expect that it can be expressed in simple algebraic form. Even if we cannot determine the accurate form of $\phi$, formula (7) is still useful since it correlates the $T$-$V$-$P$ relations of different substances.

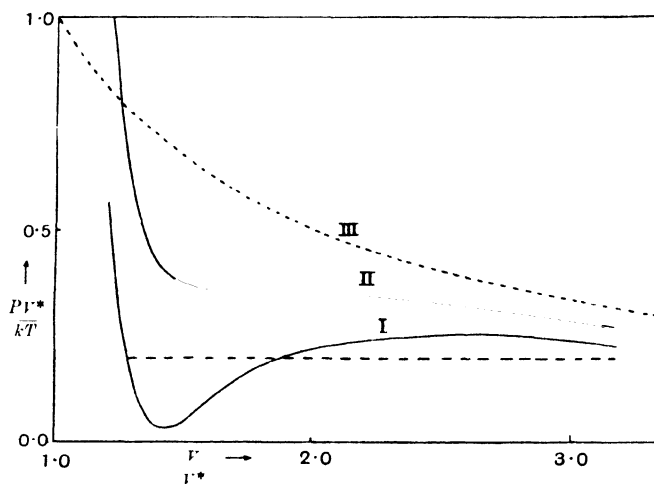



Fig. 3. Calculated isotherms. Curve II corresponds to $kT = \Lambda^*/9$, and curve I to $kT = \Lambda^*/10$ with the saturated vapour phase shown dotted. The uppermost curve is the isotherm of a perfect gas.

In fact formula (7) is an accurate general expression of the *law of corresponding states*. Any inexact empirical equation of state, such as that of van der Waals, so long as it has only two parameters, will lead to a law of corresponding states, which will be a special inexact example of (7). From the form of (7) we can deduce that the critical temperature $T_c$, critical volume $V_c$ and critical pressure $P_c$ must be related to $\Lambda^*$ and $V^*$ by

$$kT_c = \text{const.}\,\Lambda^*. \tag{809, 8}$$

$$V_c = \text{const.}\,V^*, \tag{809, 9}$$

$$P_c = \text{const.}\,\Lambda^*/V^*, \tag{809, 10}$$

$$P_c V_c/kT_c = \text{const.}, \tag{809, 11}$$

where each constant has the same value* for all substances to which the theory

* See footnote at end of chapter.

applies. Each of these constants is determined at least approximately by the calculations of Lennard-Jones and Devonshire, which we have just described.

**§ 810. Comparison with experimental data for critical point.** Since, as shown by Fig. 3, the curve II is very close to the critical one, the critical temperature $T_c$ is given by

$$kT_c = \frac{\Lambda^*}{9} = \frac{z|\epsilon^*|}{9} = \tfrac{4}{3}|\epsilon^*|, \tag{810, 1}$$

if we assume $z = 12$ corresponding to face-centred cubic packing. Taking the values of $\epsilon^*$ (for $n = 12$) given in Chapter VII, Table 4, we construct Table 5. A recent experimental study by Lark-Horowitz† of the scattering of X-rays by liquids has shown that the average value of $z$ for normal liquids is close to 11. If we use $z = 11$ instead of $z = 12$, the calculated values of $T_c$ will be decreased in the ratio 11 . 12 and the agreement with the experimental values is improved. Helium is not included in the table because the approximation of classical statistics used throughout is likely to be inaccurate. The calculated value of $T_c$ is 9·1° K. and the observed value 5·2° K.

TABLE 5

*Critical temperatures*

Values of $r^*$ and $\epsilon^*$ taken from Chapter VII, Table 4.

| Substance | $r^{*3}$ (Å$^3$) | $-\epsilon^*$ $\left(10^{-15}\,\frac{\text{ergs}}{\text{molecule}}\right)$ | $\Lambda^* = 12\lvert\epsilon^*\rvert$ $\left(10^{-15}\,\frac{\text{ergs}}{\text{molecule}}\right)$ | $\Lambda^*/9k$ $T_c$ calc. | $T_c$ obs. |
|---|---|---|---|---|---|
| $H_2$ | 35·3 | 4·25 | 51 | 41 | 33 |
| Ne | 29·2 | 4·89 | 58·6 | 47 | 44 |
| $N_2$ | 72·5 | 13·25 | 159 | 128 | 126 |
| A | 56·2 | 16·5 | 198 | 160 | 150 |

It is difficult to determine the critical volume accurately from the calculated curves without excessive labour, but from Fig. 3 it appears to be given approximately by

$$V_c \simeq 2V^* = \frac{2}{\gamma} r^{*3} = \sqrt{2}\, r^{*3}. \tag{810, 2}$$

This calculated value is rather too small. The calculated value of $P_c V_c/kT_c$ is about 0·7 whereas the experimental values are about 0·3.

An alternative method of testing the theory is a direct comparison of the calculated and observed values of the ratio $T_B/T_c$, where $T_B$ denotes the Boyle point, defined as the temperature at which the second virial coefficient

† Lark-Horowitz, Private communication.

is zero. We saw in § 714 that, for $n = 12$, the Boyle point $T_B$ is given by

$$kT_B = -3{\cdot}43\epsilon^*. \qquad (810,3)$$

Comparing (1) and (3) we obtain for the ratio $T_B/T_c$ the theoretical value

$$T_B/T_c = \tfrac{3}{4}\times 3{\cdot}43 = 2{\cdot}57. \qquad (810,4)$$

This value is compared with the experimental data in Table 6. The agreement is satisfactory except for helium and hydrogen, which cannot be expected to behave classically.

TABLE 6

*Critical temperatures $T_c$ and Boyle temperatures $T_B$*

Calculated value $T_B/T_c = 2{\cdot}57$.

| | $T_B$ | $T_c$ | $T_B/T_c$ |
|---|---|---|---|
| He | 23 | 5·2 | 4·42 |
| $H_2$ | 109 | 33·2 | 3·28 |
| Ne | 123 | 44·8 | 2·75 |
| $N_2$ | 323 | 126 | 2·56 |
| A | 410 | 150 | 2·73 |
| $O_2$ | 423 | 155 | 2·72 |
| CO | 333 | 134 | 2·5 |
| $CH_4$ | 491 | 190·5 | 2·52 |

The (unjustifiable) application of van der Waals' equation to the critical region leads to $kT_B = a/b$ and $kT_c = 8a/27b$, so that $T_B/T_c = 27/8 = 3{\cdot}4$ in much poorer agreement with the experimental values.

§ 811. **Liquid-vapour equilibrium.** We have already mentioned that the model under discussion is the more valid the greater the density, and we have seen that it is satisfactory in the neighbourhood of the critical point. At temperatures considerably below the critical point the model should be applicable *a fortiori* to the liquid phase, but not to the vapour phase. However, this is no drawback in considering the two-phase equilibrium between liquid and vapour, because the vapour will usually behave as a perfect gas, and the appropriate formulae of Chapter III can be applied to it. In particular we have for the partial potential $\mu^G$ in the vapour phase

$$\mu^G = -kT\log\frac{(2\pi mkT)^{\frac{3}{2}}}{h^3} + kT\log\frac{p}{kT} - kT\log j(T). \qquad (811,1)$$

For the liquid phase we may with sufficient accuracy neglect $PV^L$ compared with $kT$, so that (809, 1) becomes

$$\frac{\Lambda^*}{kT}\left\{2{\cdot}4\left(\frac{V^*}{V}\right)^2 - 2{\cdot}0\left(\frac{V^*}{V}\right)^4\right\} - 4\frac{\Lambda^*}{kT}\left\{\left(\frac{V^*}{V}\right)^4\frac{g_l}{g} - \left(\frac{V^*}{V}\right)^2\frac{g_m}{g}\right\} = 1. \quad (811,2)$$

Formula (2) is the equation of state of the liquid at low pressures, $PV^L \ll kT$. Since $g$, $g_l$, $g_m$ are functions of $\Lambda^*/kT$ and of $V^*/V$ only, this formula is an equation relating $\Lambda^*/kT$ to $V^*/V^L$. It can be solved by trial and error, and $V^*/V^L$ tabulated as a function of $\Lambda^*/kT$. This has been done[A] in the first two columns of Table 7. We may therefore think of $V^*/V^L$ as a determinate function of $\Lambda^*/kT$.

The partial potential $\mu^L$ in the liquid phase is obtained from (809, 5) and (808, 24). Again neglecting $PV^L$ compared with $kT$, we obtain with sufficient accuracy

$$\mu^L = -kT\log\frac{(2\pi mkT)^{\frac{3}{2}}}{h^3} - kT\log j(T) - kT - \chi_0 - kT\log(2\pi\gamma gV^L), \tag{811, 3}$$

where $\chi_0$ is given by (808, 23) and $g$ by (808, 25). The condition for equilibrium between liquid and vapour is

$$\mu^L = \mu^G. \tag{811, 4}$$

Substituting from (1) and (3) into (4) and assuming that the internal degrees of freedom are alike in the two phases, we find

$$\log p = \log\frac{kT}{2\pi\gamma gV^L} - \frac{\chi_0 + kT}{kT}, \tag{811, 5}$$

or

$$p = \frac{kT}{2\pi\gamma gV^L} e^{-(\chi_0 + kT)/kT}. \tag{811, 6}$$

It is convenient to rewrite this in the form

$$p = \frac{\Lambda^*}{V^*} Q, \tag{811, 7}$$

where $Q$ is defined by

$$\log Q = \log\frac{V^*}{2\pi\gamma gV^L} + \log\frac{kT}{\Lambda^*} - \frac{\chi_0 + kT}{kT}. \tag{811, 8}$$

Now $\chi_0$ and $g$ are explicit functions of $\Lambda^*/kT$ and $V^L/V^*$. But, as mentioned above, $V^L/V^*$ can be obtained by solution of (2) as a definite function of $\Lambda^*/kT$ and this value of $V^L/V^*$ has to be used in (8). This procedure was used by Lennard-Jones and Devonshire† to calculate the vapour pressure $p$ by (7). The results obtained by them are given in Table 7.‡

On comparing (808, 24) with (8), using (808, 23), we see that $F$ differs from $NkT\log Q$ only by terms independent of $V$. We have therefore

$$\frac{\partial \log Q}{\partial V} = \frac{PV}{kT} \simeq 0. \tag{811, 9}$$

† Lennard-Jones and Devonshire, *Proc. Roy. Soc.* A, **165**, 1 (1938).

‡ The values of $g$ given in the table were not published by Lennard-Jones and Devonshire in their paper, but they have kindly communicated the figures to us privately.

[A] See appendix, § A 7.

TABLE 7

| $\frac{\Lambda^*}{kT}$ | $\frac{V^L}{V^*}$ | $g \times 10^4$ | $Q$ | $\log_e Q$ | $1{\cdot}92 - 0{\cdot}678\frac{\Lambda^*}{kT}$ |
|---|---|---|---|---|---|
| 12·8 | 1·118 | 7·74 | $1{\cdot}16 \times 10^{-3}$ | − 6·76 | − 6·76 |
| 15·8 | 1·054 | 3·86 | $1{\cdot}59 \times 10^{-4}$ | − 8·75 | − 8·79 |
| 18·0 | 1·026 | 2·70 | $3{\cdot}52 \times 10^{-5}$ | − 10·26 | − 10·19 |
| 21·0 | 1·002 | 1·85 | $4{\cdot}48 \times 10^{-6}$ | − 12·32 | − 12 32 |

Hence for ordinary pressures log $Q$, regarded as a function of $V^*/V^L$ and of $\Lambda^*/kT$, is for any given value of $\Lambda^*/kT$ stationary with respect to $V^*/V^L$. Consequently the value of $Q(T)$ is sensitive to changes in $T$ but not to changes in $V^L$. It was found that in the range of temperatures between $\Lambda^*/kT = 12{\cdot}8$ and $\Lambda^*/kT = 21$, within the accuracy of the calculations, log $Q$ can be expressed by the relation

$$\log_e Q(\Lambda^*/kT) = 1{\cdot}92 - 0{\cdot}678\Lambda^*/kT. \qquad (811, 10)$$

The accuracy of this relation is shown by a comparison of the last two columns of Table 7. When we use the relation (10), formula (7) becomes

$$\log_e \frac{pV^*}{\Lambda^*} = 1{\cdot}92 - 0{\cdot}678\,\frac{\Lambda^*}{kT}. \qquad (811, 11)$$

Using the numerical values of $V^*$ and $\Lambda^*$ of Table 5 and using the symbol $P^\dagger$ to denote an atmosphere, we can express the vapour pressure in the form

$$p/P^\dagger = e^{(A-B/T)}, \qquad (811, 12)$$

with the numerical values given in Table 8. The boiling-point at 1 atmosphere is then equal to $B/A$. We see that there is satisfactory agreement

TABLE 8

| | $\Lambda^* = 12\lvert\epsilon^*\rvert$ $\left(10^{-15}\,\frac{\text{ergs}}{\text{molecule}}\right)$ | $V^* = r^{*3}\sqrt{2}$ (Å³ molecule) | $A$ | $B$ (deg.) | Boiling point | | Boiling-point / Critical temp. | |
|---|---|---|---|---|---|---|---|---|
| | | | | | Calc | Obs. | Calc. | Obs. |
| $H_2$ | 50 9 | 24·2 | — | — | 26·4 | 20·3 | — | — |
| Ne | 58·7 | 20·6 | 9·863 | 291·8 | 29·6 | 27·2 | 0·62 | 0·61 |
| $N_2$ | 159 | 51·3 | 9·950 | 786·3 | 79·0 | 77·2 | 0·61 | 0·61 |
| A | 199 | 38·9 | 10·407 | 979 | 94·3 | 87·4 | 0·59 | 0·58 |

between the calculated and observed values for the boiling points. If we compare the ratio of the boiling-point to the critical temperature, the agreement between calculated and observed values is even more remarkable. The theory can hardly be expected to apply to such light molecules as $H_2$,

but it may be noted that the calculated boiling-point is 26·4° as compared with the experimental value 20·3°.

**§ 812. Heat of evaporation.** For the molecular heat content in the liquid phase we have, according to (809, 4) and (809, 6),

$$H^L = \tfrac{3}{2}kT - \Lambda^*\left\{1{\cdot}2\left(\frac{V^*}{V^L}\right)^2 - 0{\cdot}5\left(\frac{V^*}{V^L}\right)^4\right\}$$
$$+\Lambda^*\left(\frac{V^*}{V^L}\right)^4\frac{g_l}{g} - 2\Lambda^*\left(\frac{V^*}{V^L}\right)^2\frac{g_m}{g} + E^{\text{int}} + PV^L, \quad (812, 1)$$

while for the molecular heat content $H^G$ in the vapour phase we have

$$H^G = \tfrac{5}{2}kT + E^{\text{int}}. \quad (812, 2)$$

By subtraction we obtain for $\Lambda_e$ the molecular heat of evaporation

$$\Lambda_e = kT + \Lambda^*\left\{1{\cdot}2\left(\frac{V^*}{V^L}\right)^2 - 0{\cdot}5\left(\frac{V^*}{V^L}\right)^4\right\} - \Lambda^*\left(\frac{V^*}{V^L}\right)^4\frac{g_l}{g} + 2\Lambda^*\left(\frac{V^*}{V^L}\right)^2\frac{g_m}{g} - PV^L$$
$$= \chi_0 + kT - \Lambda^*\left(\frac{V^*}{V^L}\right)^4\frac{g_l}{g} + 2\Lambda^*\left(\frac{V^*}{V^L}\right)^2\frac{g_m}{g} - PV^L. \quad (812, 3)$$

The term $-PV^L$ can, as usual, be neglected. Further the terms in $g_l$ and $g_m$ with their signs reversed represent the average excess potential energy of the molecule in its cell over its value at the centre of the cell. This will certainly be small compared with $\chi_0$, and an accurate evaluation of these terms seems hardly worth while. Instead we use as an approximation the value this excess potential energy would have if the molecule moved in its cell as a classical isotropic harmonic oscillator. This value according to the equipartition rule is $\tfrac{3}{2}kT$. We thus obtain in place of (3) the approximation

$$\Lambda_e = \chi_0 + kT - \tfrac{3}{2}kT = \chi_0 - \tfrac{1}{2}kT$$
$$= \Lambda^*\left\{1{\cdot}2\left(\frac{V^*}{V^L}\right)^2 - 0{\cdot}5\left(\frac{V^*}{V^L}\right)^4\right\} - \tfrac{1}{2}kT. \quad (812, 4)$$

This formula is not the most convenient one to apply, since it necessitates an accurate determination of $V^*/V^L$ by means of (811, 2). It is more convenient to combine the thermodynamic relation

$$\left(\frac{\partial \log p}{\partial T}\right)_P = \frac{\Lambda_e}{kT^2} \quad (812, 5)$$

with formula (811, 11). We thus obtain the simple result

$$\Lambda_e = 0{\cdot}678\,\Lambda^*. \quad (812, 6)$$

The entropy of evaporation (to a pressure of one atmosphere) at the boiling-point $T_b$ is given by

$$\Delta S = \frac{\Lambda_e}{T_b} = 0{\cdot}678\frac{\Lambda^*}{T_b}. \quad (812, 7)$$

We can use (810, 1) to express $\Lambda^*$ in terms of the critical temperature $T_c$, and so obtain

$$\frac{\Delta S}{k} = 0{\cdot}678 \times 9\frac{T_c}{T_b}. \qquad (812, 8)$$

From Table 8 we see that the calculated and the observed values of $T_b/T_c$ are very near to 0·60. Using this value in (8), we obtain

$$\frac{\Delta S}{k} = \frac{0{\cdot}678}{0{\cdot}60} \times 9 = 10{\cdot}3, \qquad (812, 9)$$

confirming Trouton's rule. Too much stress should not be placed on this apparent agreement, since although 10·3 is very close to the value of $\Delta S/k$ for most normal organic liquids, it must be remembered that our formulae were derived for Ne, $N_2$, A, and for these substances the experimental values of $\Delta S/k$ are only about 8 (see Table 2, last column, for $N\Lambda_e/T_b$).

Trouton's rule can be formulated as follows: all normal liquids have the same entropy of evaporation at their boiling-points. According to (811, 10) this would imply equal values of $V^*/\Lambda^*$ for all liquids. Hildebrand† has proposed the following modification of Trouton's rule: all normal liquids have the same entropy of evaporation at temperatures such that the molecular concentration of the saturated vapour has the same value. If we denote the number of molecules per unit volume of the vapour by $c^G$, we can rewrite (811, 11) as

$$\log_e c^G V^* = 1{\cdot}92 - 0{\cdot}678\Lambda^*/kT + \log_e(\Lambda^*/kT). \qquad (812, 10)$$

We thus see that Hildebrand's rule implies equal values of $V^*$ for all liquids. Actually differences in $\Lambda^*$ between different liquids are likely to be more serious than differences in $V^*$, and thus we should expect Hildebrand's rule to be an improvement on Trouton's rule, as in fact it is.‡

§ **813. Mixtures.** We now turn to the properties of mixtures of liquids, and for brevity confine ourselves almost entirely to mixtures of two types of molecule (binary mixtures), since the extension of the theory to mixtures of more than two types of molecule is straightforward. We can immediately write down a formal expression for the free energy of a mixture of two such liquids. It is in fact the same as formula (701, 10) for mixtures of imperfect gases, namely

$$F = -N_A kT \log \phi_A(T) - N_B kT \log \phi_B(T) - kT \log \Omega(T), \quad (813, 1)$$

† Hildebrand, *J. Am. Chem. Soc.* **37**, 970 (1915); **40**, 45 (1918).

‡ In a very recent paper, *J. Chem. Phys.* **7**, 233 (1939), Hildebrand discusses the accuracy of his rule and the causes of deviations from it.

where $\phi(T)$ is defined for each species by

$$\phi(T) = \frac{(2\pi mkT)^{\frac{3}{2}}}{h^3} j(T), \tag{813, 2}$$

and $\Omega(T)$ is defined by

$$\Omega(T) = \frac{1}{N_A!\,N_B!}\int\!\dots\!\int e^{-W/kT}\,(d\omega_A)^{N_A}\,(d\omega_B)^{N_B}. \tag{813, 3}$$

Here $W$ as usual is the configurational potential energy, and the integral is extended over all configurations of the $N_A$ molecules $A$ and the $N_B$ molecules $B$ of different types. Formula (1) is perfectly general, provided that the internal degrees of freedom can be separated from the configurational degrees of freedom, and that the latter are effectively classical. The problem for mixtures, like the problem for pure liquids, is thus reduced to that of evaluating $\Omega(T)$. We shall suppose that for each of the pure liquids the problem of evaluating $\Omega(T)$, and so all the equilibrium properties, has been at least approximately solved, and shall endeavour to express the equilibrium properties of the mixture in terms of those of the single liquids. To succeed it is always necessary to make some further assumptions; we shall consider various types of mixtures such as regular solutions, perfect solutions, ideal dilute solutions, these designations referring to the particular type of assumption made concerning the mixture.

**§ 814. Strictly regular solutions.** For a single normal liquid we have seen in § 802 that $\Omega(T)$ can be expressed in the form

$$\Omega(T) = \{Nve^{\chi_0/kT}\}^N/N! = \{eve^{\chi_0/kT}\}^N, \tag{814, 1}$$

where $v$ denotes an effectively free volume per molecule and $-\chi_0$ a molecular energy. In the over-simplified smoothed potential model $v$ and $\chi_0$ are functions of the molecular volume $V$, but are independent of the temperature. In any more refined approximation $v$ varies with the temperature, but for our present purpose this temperature dependence is not serious.

Let us now consider a mixture of molecules of two types $A$ and $B$, and assume firstly that both types pack in the same way so that they have a common value of $z$, e.g. $z = 12$, corresponding to face-centred cubic packing. Let us assume secondly that the molecular volumes $V$ are sufficiently alike, so that a mixture of the two kinds of molecules can also pack in the same way as each of the single liquids. For spherical molecules this assumption requires* a ratio of the molecular volumes between 1 and 2 or a ratio of the diameters between 1 and 1·26, and will be fulfilled for many pairs of liquids. Thirdly, we assume that the ratio of the free volumes $v$ of the two pure liquids does not differ from unity by more than about 30 %. We assume fourthly that,

* Private communication from Professor Bernal.

when the two liquids are mixed at a given temperature and given pressure, the molecular volumes $V_A$, $V_B$ and the free volumes $v_A$, $v_B$ of both remain unaltered. Fifthly, we assume that in any given configuration of volume $V$ satisfying the relation

$$V = N_A V_A + N_B V_B \tag{814, 2}$$

the potential energy $W$ may be regarded as the sum of contributions from pairs of closest neighbours. We shall refer to mixtures with these properties as *strictly regular solutions.**

We would mention in passing that the treatment which we are going to give of regular solutions should apply just as well to solid mixtures as to liquid mixtures, if not better. We shall refer to this application of the theory to mixed crystals in § 1315.

Let $\chi_A$ and $\chi_B$ denote the values of $\chi_0$ in the two pure liquids respectively. Then since in the single liquid $A$ each molecule has an average potential energy $-\chi_A$ and has $z$ closest neighbours, we may regard $-2\chi_A/z$ as the average energy of interaction of two $A$ molecules. Similarly the average energy of interaction of two $B$ molecules is $-2\chi_B/z$. Let us define a mixing energy $w_{AB}$ such that, if we start with the two pure liquids and interchange an interior $A$ molecule with an interior $B$ molecule, the total increase of potential energy is $2w_{AB}$. In this process we destroy $z$ pairs $AA$ and $z$ pairs $BB$ and create $2z$ pairs $AB$. Hence by the definition of $w_{AB}$, the average potential energy of an $AB$ pair is

$$(-2\chi_A - 2\chi_B + 2w_{AB})/2z = (-\chi_A - \chi_B + w_{AB})/z.$$

Now consider a particular configuration of the mixture of $N_A$ molecules $A$ and $N_B$ molecules $B$, in which the number of $AB$ pairs of closest neighbours is $zX$. Then the number of neighbours of $A$ molecules which are not $B$'s is $z(N_A - X)$, and the number of $AA$ pairs is $\frac{1}{2}z(N_A - X)$; the number of $BB$ pairs is $\frac{1}{2}z(N_B - X)$, the total number of pairs of all three kinds being $\frac{1}{2}z(N_A + N_B)$. For this particular configuration the total potential energy $W$ is therefore given by

$$\begin{aligned} W &= \tfrac{1}{2}z(N_A - x)(-2\chi_A/z) + \tfrac{1}{2}z(N_B - x)(-2\chi_B/z) + zX(-\chi_A - \chi_B + w_{AB})/z \\ &= -N_A\chi_A - N_B\chi_B + Xw_{AB}. \end{aligned} \tag{814, 3}$$

If we substitute (3) into (813, 3), we obtain

$$\Omega(T) = e^{(N_A\chi_A + N_B\chi_B)/kT} \frac{1}{N_A!\,N_B!} \int \dots \int e^{-Xw_{AB}/kT} (d\omega_A)^{N_A} (d\omega_B)^{N_B}. \tag{814, 4}$$

Before attempting the further reduction of $\Omega(T)$ we shall consider a simple special case.

* The expression *regular solutions* is due to Hildebrand, *J. Am. Chem. Soc.* **51**, 66 (1929), who, however, applied it to solutions of a type slightly more general than corresponds to the above assumptions. Such solutions have not yet proved susceptible to accurate analysis.

§ **815. Perfect solutions.** We define a *perfect solution* as a mixture having all the properties of a strictly regular solution with the further property that $w_{AB} = 0$. According to the definition of $w_{AB}$ there is then no change of potential energy when an $A$ molecule surrounded by other $A$ molecules is interchanged with a $B$ molecule surrounded by other $B$ molecules. Consequently any two perfect solutions of $A$ and $B$ will mix at constant temperature and pressure without any energy change. For a perfect solution formula (814, 4) reduces to

$$\Omega(T) = e^{(N_A\chi_A+N_B\chi_B)/kT}\frac{1}{N_A!\,N_B!}\int\ldots\int (d\omega_A)^{N_A}(d\omega_B)^{N_B}$$

$$= e^{(N_A\chi_A+N_B\chi_B)/kT}\frac{1}{N_A!\,N_B!}(N_A v_A + N_B v_B)^{N_A+N_B}. \quad (815, 1)$$

Our third assumption in defining strictly regular solutions, of which perfect solutions are a particular class, was that the ratio $v_A$ to $v_B$ differed from unity by not more than 30 %. This being so the arithmetic mean of a number $N_A$ of $v_A$'s and $N_B$ of $v_B$'s will differ from the geometric mean by not more than about 1 %. We may therefore use the approximation

$$\frac{N_A v_A + N_B v_B}{N_A + N_B} = (v_A^{N_A} v_B^{N_B})^{1/(N_A+N_B)}. \quad (815, 2)$$

Using this approximation in (1), we obtain

$$\Omega(T) = (ev_A e^{\chi_A/kT})^{N_A}(ev_B e^{\chi_B/kT})^{N_B}(N_A+N_B)!/N_A!\,N_B!. \quad (815, 3)$$

Now using this value of $\Omega(T)$ in (813, 1), we have

$$F = N_A\left\{-\chi_A - kT\log(\phi_A v_A) - kT + kT\log\frac{N_A}{N_A+N_B}\right\}$$

$$+ N_B\left\{-\chi_B - kT\log(\phi_B v_B) - kT + kT\log\frac{N_B}{N_A+N_B}\right\}. \quad (815, 4)$$

The Gibbs function $G$ is therefore

$$G = F + PV = F + P(N_A V_A + N_B V_B) \simeq F \quad (815, 5)$$

at ordinary pressures. Now $\chi_A$, $v_A$ are functions of $T$, $V_A$, and $\chi_B$, $v_B$ are functions of $T$, $V_B$. Hence $\chi_A$, $\chi_B$, $v_A$, $v_B$ are independent of $N_A$, $N_B$ at constant $T$, $V_A$, $V_B$ which means at constant $T$, $P$ rather than at constant $T$, $V$. It is therefore simpler to derive the partial potentials $\mu_A$, $\mu_B$ from $G$ rather than from $F$. We obtain

$$\mu_A = \left(\frac{\partial G}{\partial N_A}\right)_{T,P} = \left(\frac{\partial G}{\partial N_A}\right)_{T,V_A,V_B}$$

$$= -\chi_A - kT\log(\phi_A v_A) - kT + kT\log\frac{N_A}{N_A+N_B}, \quad (815, 6)$$

and similarly

$$\mu_B = -\chi_B - kT\log(\phi_B v_B) - kT + kT\log\frac{N_B}{N_A+N_B}. \qquad (815, 7)$$

If we denote the partial potentials of $A$ and $B$ in the pure liquids at the given temperature and pressure by $\mu_A^0$ and $\mu_B^0$ respectively, we can rewrite (6) and (7) in the form

$$\mu_A = \mu_A^0 + kT\log\frac{N_A}{N_A+N_B}, \qquad (815, 8)$$

$$\mu_B = \mu_B^0 + kT\log\frac{N_B}{N_A+N_B}. \qquad (815, 9)$$

We can derive a formula for the entropy from (4) and (5) by differentiating with respect to $T$. The result can be expressed in the form

$$S = N_A S_A^0 + N_B S_B^0 + k\left\{N_A\log\frac{N_A+N_B}{N_A} + N_B\log\frac{N_A+N_B}{N_B}\right\}, \qquad (815, 10)$$

where $S_A^0$ and $S_B^0$ are the entropies of the unmixed components. We define the *entropy of mixing* $\Delta S$ as the excess of the entropy of a solution over that of the two unmixed components *at the same temperature and pressure.* We thus see from (10) that for a perfect solution the entropy of mixing is given by

$$\Delta S = k\left\{N_A\log\frac{N_A+N_B}{N_A} + N_B\log\frac{N_A+N_B}{N_B}\right\}. \qquad (815, 11)$$

From (4) and (5) we see that the analogous *free energy of mixing* $\Delta F$ and *Gibbs function of mixing* $\Delta G$ are given by

$$\Delta F = \Delta G = -kT\left\{N_A\log\frac{N_A+N_B}{N_A} + N_B\log\frac{N_A+N_B}{N_B}\right\}. \qquad (815, 12)$$

Finally for the analogous *energy of mixing* $\Delta E$ and *total heat of mixing* $\Delta H$ we have

$$\Delta E = \Delta H = \Delta F + T\Delta S = 0, \qquad (815, 13)$$

which is physically obvious from the condition $w_{AB} = 0$ by which a perfect solution was defined.

## § 816. Raoult's law for perfect solutions.

The vapour pressure is obtained, as usual, by equating the partial potentials in the liquid and vapour phases. We denote the partial vapour pressures over the perfect solution by $p_A$, $p_B$, the vapour pressures of the two pure liquids at the same temperature and pressure by $p_A^0$, $p_B^0$, and recall that in formula (811, 1) for the partial potential $\mu^G$ in the gas the only term dependent on the con-

centration (partial pressure) is $kT \log p$. Hence by applying (815, 7) to the solution and to the pure liquid $\alpha$ and subtracting, we obtain

$$kT \log \frac{p_A}{p_A^0} = kT \log \frac{N_A}{N_A + N_B}, \tag{816, 1}$$

or

$$p_A = p_A^0 \frac{N_A}{N_A + N_B}, \tag{816, 2}$$

which is Raoult's law for the species $A$. The species $B$ similarly obeys Raoult's law in the same form. This law tells us that when the vapour pressure of either component of a perfect solution is plotted against the molecular fraction a straight line is obtained. Experimentally this law is verified for certain pairs of chemically similar substances, for example of ethylene bromide and propylene bromide.*

§ 817. **Strictly regular solutions** (cont.). We return now to the more general case of strictly regular solutions for which the mixing energy $w_{AB}$ is not zero. $\Omega(T)$ is now given by (814, 4). If we define a quantity $\bar{\bar{X}}$ by the relation

$$e^{-\bar{\bar{X}} w_{AB}/kT} \int \dots \int (d\omega_A)^{N_A} (d\omega_B)^{N_B} = \int \dots \int e^{-X w_{AB}/kT} (d\omega_A)^{N_A} (d\omega_B)^{N_B}, \tag{817, 1}$$

and evaluate the integral on the left as in § 815, we obtain

$$\Omega(T) = (ev_A e^{\chi_A/kT})^{N_A} (ev_B e^{\chi_B/kT})^{N_B} \frac{(N_A + N_B)!}{N_A! \, N_B!} e^{-\bar{\bar{X}} w_{AB}/kT}. \tag{817, 2}$$

Substituting this into (813, 1), we obtain

$$F = N_A \left\{ -\chi_A - kT \log(\phi_A v_A) - kT + kT \log \frac{N_A}{N_A + N_B} \right\}$$

$$+ N_B \left\{ -\chi_B - kT \log(\phi_B v_B) - kT + kT \log \frac{N_B}{N_A + N_B} \right\} + \bar{\bar{X}} w_{AB}. \tag{817, 3}$$

It is convenient to denote by $F'$, $G'$, $E'$, $H'$, $S'$ the excess of the values of the corresponding functions over the values given by the formulae for perfect solutions. It is then easily verified that at ordinary low pressures

$$G' = F' = \bar{\bar{X}} w_{AB}, \tag{817, 4}$$

$$H' = E' = \bar{\bar{X}} w_{AB} - T \left( \frac{\partial [\bar{\bar{X}} w_{AB}]}{\partial T} \right)_{v_A, v_B, N_A, N_B}. \tag{817, 5}$$

$$S' = -\left( \frac{\partial [\bar{\bar{X}} w_{AB}]}{\partial T} \right)_{v_A, v_B, N_A, N_B}. \tag{817, 6}$$

Whereas $\chi_A$, $\chi_B$ may vary appreciably with the temperature, the differential

* Zawidski, *Z. Physikal. Chem.* **35**, 128 (1900).

quantity $w_{AB}$ will vary with the temperature only in so far as the change of tightness of packing will affect the $AB$ interaction energy differently from the $AA$ and $BB$ interaction energies. We may reasonably expect this differential effect to be small, and we shall therefore treat $w_{AB}$ as independent of temperature. We then replace (5) and (6) by

$$H' = E' = \left(\bar{\bar{X}} - T\frac{\partial \bar{\bar{X}}}{\partial T}\right) w_{AB}, \tag{817,7}$$

$$S' = -\frac{\partial \bar{\bar{X}}}{\partial T} w_{AB}. \tag{817,8}$$

If we denote by $\bar{X}$ the equilibrium value of $X$, we have, as usual,

$$\bar{X}\int \dots \int e^{-Xw_{AB}/kT}(d\omega_A)^{N_A}(d\omega_B)^{N_B} = \int \dots \int X e^{-Xw_{AB}/kT}(d\omega_A)^{N_A}(d\omega_B)^{N_B}; \tag{817,9}$$

by differentiating (1) we can verify that $\bar{\bar{X}}$ and $\bar{X}$ are related by

$$\bar{X} = \bar{\bar{X}} - T\frac{\partial \bar{\bar{X}}}{\partial T} = \frac{\partial(\bar{\bar{X}}/T)}{\partial(1/T)}. \tag{817,10}$$

Using (10) in (7) we obtain

$$H' = E' = \bar{X} w_{AB}, \tag{817,11}$$

a result which should be physically obvious. The problem of computing the free energy, and so all the equilibrium properties, is thus reduced to that of determining $\bar{\bar{X}}$, or alternatively $\bar{X}$, since the two are interrelated by (10). We shall consider two attempts to compute them theoretically.

§ 818. **Crude treatment of regular solutions.** Early attempts to evaluate the deviations of actual solutions from perfect solutions were made by several authors.* In these attempts the assumptions made were in every case equivalent to putting

$$\bar{X}^2 = (N_A - \bar{X})(N_B - \bar{X}). \tag{818,1}$$

Since on this approximation $\bar{X}$ is independent of $T$, we have according to (817, 10)

$$\bar{X} = \bar{\bar{X}}, \tag{818,2}$$

and according to (817, 8)

$$S' = 0. \tag{818,3}$$

The physical meaning of this assumption, that the change of entropy on mixing is the same as for an ideal solution, is completely random mixing. Although such an assumption cannot be accurate, we shall discuss its consequences because they can be expressed in very simple formulae, and

* Porter, *Trans. Fara. Soc.* **16**, 336 (1920). Van Laar and Lorenz, *Z. anorg. Chem.* **145**, 239 (1925). Heitler, *Ann. d. Phys.* **80**, 629 (1926). Hildebrand, *J. Am. Chem. Soc.* **51**, 69 (1929). Scatchard, *Chem. Rev.* **8**, 321 (1931).

quantitatively do not differ seriously from the more complicated formulae obtained in § 819 from more accurate assumptions.

Solving (1) for $\bar{X}$ and using (2), we obtain

$$\bar{\bar{X}} = \bar{X} = N_A N_B/(N_A + N_B), \tag{818, 4}$$

and consequently

$$G' = F' = H' = E' = \frac{N_A N_B}{N_A + N_B} w_{AB}. \tag{818, 5}$$

Using $\mu'_A$, $\mu'_B$ to denote the extra terms in the partial potentials due to deviations from the laws of perfect solutions, we obtain

$$\mu'_A = \frac{\partial G'}{\partial N_A} = \left(\frac{N_B}{N_A + N_B}\right)^2 w_{AB}, \tag{818, 6}$$

$$\mu'_B = \frac{\partial G'}{\partial N_B} = \left(\frac{N_A}{N_A + N_B}\right)^2 w_{AB}. \tag{818, 7}$$

The partial vapour pressures are derived, exactly as for perfect solutions, by equating the partial potentials in the liquid and gas phases. We thus obtain, in place of formula (816, 2) expressing Raoult's law for perfect solutions,

$$p_A = p_A^0 \frac{N_A}{N_A + N_B} \exp\left\{\frac{w_{AB}}{kT}\left(\frac{N_B}{N_A + N_B}\right)^2\right\}, \tag{818, 8}$$

$$p_B = p_B^0 \frac{N_B}{N_A + N_B} \exp\left\{\frac{w_{AB}}{kT}\left(\frac{N_A}{N_A + N_B}\right)^2\right\}. \tag{818, 9}$$

In Fig. 4 $p_A/p_A^0$ and $p_B/p_B^0$ have been plotted against the molecular fraction of $B$ for one negative* and three positive values of $w_{AB}/kT$. As the value of $|w_{AB}|/kT$ is increased, so do the deviations of the curves from the straight lines corresponding to Raoult's law. When $w_{AB}/kT = 2$, the curves have a horizontal point of inflexion at the composition of an equimolecular mixture. For still higher positive values of $w_{AB}/kT$ the curves have a maximum and a minimum. The middle part of the curves corresponds to unstable phases; these split into two phases such that the partial vapour pressure of each component has the same value in both phases. Since the curves for $p_A/p_A^0$ and $p_B/p_B^0$ are mirror images of each other about the abscissa corresponding to the molecular fraction $\frac{1}{2}$, the two phases in equilibrium with each other must have the compositions given by the two outer intersections of the two curves. These are the points marked $L$, $M$ in the diagram. The parts of the curves between $L$ and $M$ refer to an unrealizable single unstable phase and are therefore dotted. It can be verified that the value of the Gibbs

* The present treatment is valid equally for positive and negative values of $w_{AB}$, provided $w_{AB}/kT \geqslant -2$. When $w_{AB} < -2$ one ought to consider the possibility of the occurrence of long-range order described in detail in Chapter XIII. However, its actual occurrence seems unlikely in a liquid although it may be important in the application of the theory to solid solutions.

function $G$ for any such unstable phase is greater than the value for the sum of the two phases $L$ and $M$ into which it splits. The horizontal point of inflexion in the second curve represents the condition called *critical mixing* and the temperature corresponding to this curve is called the temperature of critical mixing. We postpone consideration of the applicability of these curves to experimental data until we have discussed the more accurate formulae obtained when formula (1) is replaced by a more correct assumption.

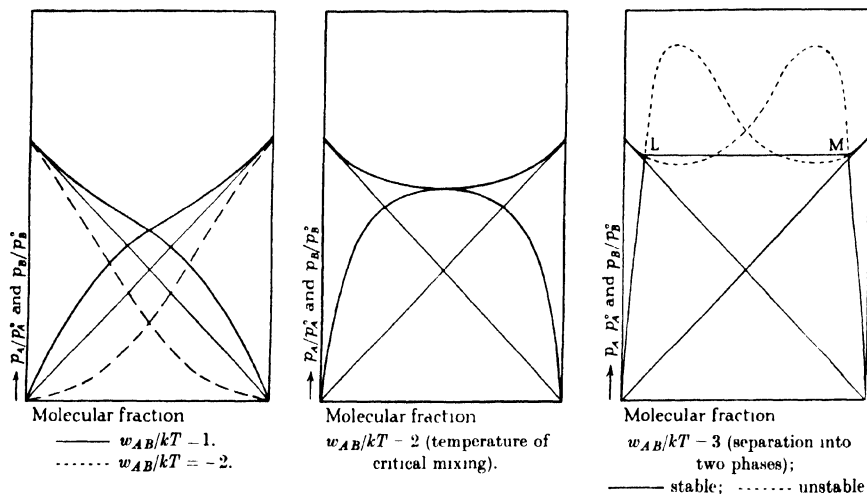



Fig. 4. Partial vapour pressures of strictly regular solutions according to crude approximation.

## § 819. Refined treatment of strictly regular solutions.

The assumption (818, 1) corresponding to completely random mixing cannot be strictly correct. By definition $\bar{X}$ must be a function of $N_A$, $N_B$ and $w_{AB}/kT$, and so for given $N_A$, $N_B$ a function of $w_{AB}/kT$. In particular when $w_{AB}/kT = \infty$, $\bar{X} = 0$; when $w_{AB}/kT = 0$, $\bar{X}$ satisfies (818, 1); when $w_{AB}/kT = -\infty$, $\bar{X}$ is equal to the lesser of $N_A$ and $N_B$. It seems obvious that $\bar{X}$ increases steadily as $w_{AB}/kT$ decreases from $+\infty$ to $-\infty$. For a given non-zero value of $w_{AB}$, $\bar{X}$ cannot be independent of $T$.

It will be shown that the formula

$$\bar{X}^2 = (N_A - \bar{X})(N_B - \bar{X})\, e^{-2w_{AB}/zkT} \qquad (819, 1)$$

is an improvement on (818, 1). Since $2w_{AB}/z$ is the energy required to change an $AA$ pair and a $BB$ pair into two $AB$ pairs, and $\bar{X}$, $(N_A - \bar{X})$, $(N_B - \bar{X})$ are proportional to the number of $AB$, $AA$ and $BB$ pairs respectively, (1) is an

equation of the form to be expected by analogy with the law of mass action for a chemical equilibrium. A strict derivation of formula (1) was first given by Rushbrooke,* but as the algebra is rather long we have relegated such a proof to a separate section (§ 820). Anticipating its proof, we shall make use of formula (1) to derive the equilibrium properties of strictly regular solutions.

On solving (1) for $\bar{X}$, we obtain

$$\frac{\bar{X}}{N_A+N_B} = \frac{\beta-1}{2(e^{2w_{AB}/zkT}-1)}, \tag{819, 2}$$

where for brevity we have introduced a quantity $\beta$ defined by

$$\beta = \{1+4N_A N_B(e^{2w_{AB}/zkT}-1)/(N_A+N_B)^2\}^{\frac{1}{2}}. \tag{819, 3}$$

Formula (2) can be transformed to

$$\bar{X} = \frac{N_A N_B}{N_A+N_B}\frac{2}{\beta+1}, \tag{819, 4}$$

a form convenient for comparison with the crude approximation of formula (818, 4).

We can now obtain a formula for $\bar{\bar{X}}$ by substituting from (4) into (817, 10) and integrating. We have

$$\bar{\bar{X}} = \frac{N_A N_B}{N_A+N_B}\frac{zkT}{2w_{AB}}\int_0^{2w_{AB}/zkT}\frac{2}{\beta+1}\,d\left(\frac{2w_{AB}}{zkT}\right), \tag{819, 5}$$

the lower limit of integration being determined by the following considerations. As $T\to\infty$ we must have a random distribution of molecular pairs, for which $\bar{\bar{X}}\sim\bar{X}$ remaining finite. Therefore $\bar{\bar{X}}/T$ vanishes as $1/T\to 0$. It is convenient to use the variable $\beta$ and the mole fraction $x$ of $A$ defined by

$$x = N_A/(N_A+N_B). \tag{819, 6}$$

According to (3) we have

$$e^{2w_{AB}/zkT} = \frac{\beta^2-(1-2x)^2}{4x(1-x)}, \tag{819, 7}$$

$$d\left(\frac{2w_{AB}}{zkT}\right) = \frac{2\beta\,d\beta}{(\beta-1+2x)(\beta+1-2x)}. \tag{819, 8}$$

Substituting from (8) into (5) and performing the integration, we find

$$\begin{aligned}\frac{\bar{\bar{X}}}{N_A+N_B} &= x(1-x)\frac{zkT}{2w_{AB}}\int_1^{\beta}\frac{4\beta\,d\beta}{(\beta-1+2x)(\beta+1-2x)(\beta+1)}\\ &= \frac{zkT}{2w_{AB}}\left\{x\log\frac{\beta-1+2x}{2x}+(1-x)\log\frac{\beta+1-2x}{2(1-x)}-\log\frac{\beta+1}{2}\right\}.\end{aligned} \tag{819, 9}$$

* Rushbrooke, *Proc. Roy. Soc.* A, **166**, 296 (1938).

The excess of the values of $F$ and $G$ over the values given by the formulae for perfect solutions are therefore

$$F' = G' = \overline{\overline{X}} w_{AB}$$

$$= (N_A + N_B)\,\tfrac{1}{2}zkT\left\{x\log\frac{\beta-1+2x}{x(\beta+1)} + (1-x)\log\frac{\beta+1-2x}{(1-x)(\beta+1)}\right\}. \quad (819, 10)$$

We obtain the corresponding contribution $\mu'_A$ of $w_{AB}$ to the partial potential $\mu_A$ from the relation

$$\mu'_A = (\partial G'/\partial N_A)_{T,N_B}. \quad (819, 11)$$

In using (11) we have to remember that $\beta$ and $x$ are functions of $N_A$, $N_B$. The algebra is straightforward but rather long; the final result obtained is

$$\frac{\mu'_A}{kT} = \tfrac{1}{2}z\log\frac{\beta-1+2x}{x(\beta+1)}. \quad (819, 12)$$

If we add to (12) the terms for a perfect solution, we obtain

$$\frac{\mu_A - \mu_A^0}{kT} = \log x + \tfrac{1}{2}z\log\frac{\beta-1+2x}{x(\beta+1)}, \quad (819, 13)$$

where $\mu_A^0$ denotes the partial potential of the pure liquid $A$. The corresponding formula for the partial vapour pressure is

$$\frac{p_A}{p_A^0} = x\left\{\frac{\beta-1+2x}{x(\beta+1)}\right\}^{\frac{1}{2}z}. \quad (819, 14)$$

In any of these formulae we can substitute for $\beta$ from (3) and expand in powers of $w_{AB}/zkT$. If we neglect all powers of $w_{AB}/zkT$ above the first, we recover the formulae of the crude approximation given in § 818. The behaviour of the partial potentials and partial vapour pressures according to the more accurate treatment is generally similar to that according to the crude treatment. At low temperatures mixtures of certain compositions become unstable and split into two phases. This will occur when there exist mixtures for which

$$\partial\mu_A/\partial x < 0 \quad (819, 15)$$

or alternatively

$$\partial p_A/\partial x < 0. \quad (819, 16)$$

From Fig. 4, which is at least qualitatively correct, the critical point is determined by the conditions

$$\partial p_A/\partial x = 0, \quad \partial^2 p_A/\partial x^2 = 0, \quad (819, 17)$$

equivalent to

$$\partial\mu_A/\partial x = 0, \quad \partial^2\mu_A/\partial x^2 = 0. \quad (819, 18)$$

Owing to the symmetry of $G'$ about $x = \tfrac{1}{2}$ this critical point must occur at $x = \tfrac{1}{2}$. This can be verified *a posteriori*, but the algebra is considerably simplified by the knowledge that the solution of (17) or (18) occurs at

$x = \frac{1}{2}$. When $x = \frac{1}{2}$ one has $\beta = e^{w_{AB}/zkT}$ and according to (13)

$$\frac{\mu_A - \mu''_A}{kT} = \log \tfrac{1}{2} - \tfrac{1}{2}z \log \tfrac{1}{2}(1 + e^{-w_{AB}/zkT}) \quad (x = \tfrac{1}{2}), \qquad (819, 19)$$

$$\frac{1}{kT}\frac{\partial \mu_A}{\partial x} = 2 - z + ze^{-w_{AB}/zkT} \quad (x = \tfrac{1}{2}), \qquad (819, 20)$$

$$\frac{1}{kT}\frac{\partial^2 \mu_A}{\partial x^2} = -4 + 2z - 2ze^{-w_{AB}/zkT} \quad (x = \tfrac{1}{2}). \qquad (819, 21)$$

From (20) and (21) we can verify that the equations (18) are simultaneously satisfied by $x = \frac{1}{2}$ at a critical temperature $T_c$ determined by

$$\frac{w_{AB}}{kT_c} = z \log \frac{z}{z-2}. \qquad (819, 22)$$

On expansion in powers of $w_{AB}/zkT$ we find that the leading terms of $F'$ (or $G'$) and $E'$ (or $H'$) are equal and the corresponding term in $S'$ vanishes. Consequently the crude assumption $S' = 0$ used in § 818 leads to formulae which are useful approximations to those of the present section. The formulae of the present section have not been tested on experimental data, but the simpler formulae of the crude theory have been found to fit the experimental data at least approximately. For example Porter† showed that the partial vapour pressures of mixtures of acetone and ether at 30° C. can be expressed by formulae (818, 8), (818, 9), if $w_{AB}/kT$ is given the value 0·741. For this particular mixture, and others considered by Porter, since $w_{AB}/kT < 2$, there is no separation into two phases. Hildebrand* has successfully applied formulae (818, 8), (818, 9) with values of $w_{AB}/kT > 2$ to pairs of liquids that are only partially miscible.

There is a scarcity of data sufficiently accurate to distinguish between formula (818, 8) and formula (9), especially when there is an adjustable parameter $w_{AB}$. It is also questionable whether the difference between the two formulae is not less than an entirely different inaccuracy due to differences in the sizes and packing of the two molecular species. We must not forget that all our formulae are dependent on the assumption that the two kinds of molecules are sufficiently alike in size to be interchangeable in the liquid phases. In § 821 we shall refer briefly to the only useful attempts that have been made to calculate the behaviour of a mixture of molecules of greatly different sizes.

**§ 820. Derivation of equation for $\bar{X}$.** In the previous section we assumed the quasi-chemical equilibrium condition (819, 1) and this still awaits proof. It has been shown by Rushbrooke‡ that this, and in fact all

* Hildebrand, *Solubility of Non-electrolytes* (Reinhold, 1936).

† Porter, *Trans. Fara. Soc.* **16**, 339 (1920).

‡ Rushbrooke, *Proc. Roy. Soc.* A. **166**, 296 (1938).

the equilibrium properties of regular solutions, can conveniently be derived by the use of the grand partition function. We shall give an abridged and simplified version of Rushbrooke's derivation, using the method outlined in §§ 608–610, the arguments of which we repeat here in the notation of the present problem.

It is convenient to modify the notation used hitherto. The ordinary partition function $f(T)$ for the whole assembly consisting of $N_A$ molecules $A$ and $N_B$ molecules $B$, treated as a single system, can be written in the form

$$f(T) = \Sigma_{N_{AB}} g(N_A, N_B, N_{AB})\, e^{-N_{AB}w_{AB}/zkT}\{\phi_A v_A e^{(\chi_A+kT)/kT}\}^{N_A} \times \{\phi_B v_B e^{(\chi_B+kT)/kT}\}^{N_B}, \quad (820, 1)$$

where $N_{AB}$ denotes the number of $AB$ pairs of neighbours and $g(N_A, N_B, N_{AB})$ denotes the number of distihguishable arrangements of the $N_A$ molecules $A$ and $N_B$ molecules $B$ with the specified value of $N_{AB}$. It is to be noted that the exponential factors are $e^{(\chi_A+kT)/kT}$ and $e^{(\chi_B+kT)/kT}$, not $e^{\chi_A/kT}$ and $e^{\chi_B/kT}$. The extra factor $e$ per molecule represents the difference between a liquid and a crystal, as explained in § 803. The coefficients $g(N_A, N_B, N_{AB})$ have to satisfy the relation

$$\Sigma_{N_{AB}} g(N_A, N_B, N_{AB}) = (N_A + N_B)!/\{N_A!\, N_B!\}. \quad (820, 2)$$

With this notation the quantities $\overline{\overline{N_{AB}}} = z\overline{\overline{X}}$ and $\overline{N_{AB}} = z\overline{X}$ are defined by

$$e^{-\overline{\overline{N_{AB}}}w_{AB}/zkT}(N_A + N_B)!/\{N_A!\, N_B!\} = \Sigma_{N_{AB}} g(N_A, N_B, N_{AB})\, e^{-N_{AB}w_{AB}/zkT}, \quad (820, 3)$$

$$\overline{N_{AB}}\, \Sigma_{N_{AB}} g(N_A, N_B, N_{AB})\, e^{-N_{AB}w_{AB}/zkT} = \Sigma_{N_{AB}} N_{AB}\, g(N_A, N_B, N_{AB})\, e^{-N_{AB}w_{AB}/zkT}. \quad (820, 4)$$

If we substitute (3) into (1) we obtain for the free energy $F$ of the assembly

$$\frac{F}{kT} = -\log f(T) = -(N_A + N_B)\log(N_A + N_B) + N_A \log N_A + N_B \log N_B + \overline{\overline{N_{AB}}} w_{AB}/zkT - N_A \log(\phi_A v_A) - N_A(\chi_A + kT)/kT - N_B \log(\phi_B v_B) - N_B(\chi_B + kT)/kT, \quad (820, 5)$$

in agreement with (817, 3), since $\overline{\overline{N_{AB}}}/z = \overline{\overline{X}}$.

Corresponding to formula (1) for the ordinary partition function for given $N_A$, $N_B$, the grand partition function for given $\lambda_A$, $\lambda_B$ is

$$\Xi = \Sigma_{N_A,N_B} \Sigma_{N_{AB}} g(N_A, N_B, N_{AB})\, e^{-N_{AB}w_{AB}/zkT}(\phi_A v_A e^{(\chi_A+kT)/kT})^{N_A} \times (\phi_B v_B e^{(\chi_B+kT)/kT})^{N_B} \lambda_A^{N_A} \lambda_B^{N_B}. \quad (820, 6)$$

For brevity we write

$$\xi_A = \lambda_A \phi_A v_A e^{(\chi_A+kT)/kT}, \quad \xi_B = \lambda_B \phi_B v_B e^{(\chi_B+kT)/kT}, \quad (820, 7)$$

$$\eta_{AB} = e^{-w_{AB}/zkT}, \quad (820, 8)$$

so that (6) becomes

$$\Xi = \Sigma_{N_A, N_B} \Sigma_{N_{AB}} g(N_A, N_B, N_{AB})\, \eta_{AB}^{N_{AB}} \xi_A^{N_A} \xi_B^{N_B}. \tag{820, 9}$$

Then for the given values of $T$, $\lambda_A$, $\lambda_B$ the frequency of a configuration of specified $N_A$, $N_B$ and $N_{AB}$ is proportional to the term in $\Xi$ with these values of $N_A$, $N_B$ and $N_{AB}$. It follows that the average values of $N_A$, $N_B$ and $N_{AB}$ are given by the equations

$$\overline{N_A} = \xi_A \frac{\partial \log \Xi}{\partial \xi_A}, \quad \overline{N_B} = \xi_B \frac{\partial \log \Xi}{\partial \xi_B}, \tag{820, 10}$$

$$\overline{N_{AB}} = \eta_{AB} \frac{\partial \log \Xi}{\partial \eta_{AB}}. \tag{820, 11}$$

Exactly as for perfect mixed crystals discussed in § 606, we may always without appreciable error replace $\Xi$ by its greatest term, say $\Xi_{(N^*)}$, given by

$$\Xi_{(N^*)} = g(N_A^*, N_B^*, N_{AB}^*)\, \eta_{AB}^{N_{AB}^*} \xi_A^{N_A^*} \xi_B^{N_B^*}, \tag{820, 12}$$

and it then follows that

$$\overline{N_A} = N_A^*, \quad \overline{N_B} = N_B^*, \tag{820, 13}$$

$$\overline{N_{AB}} = N_{AB}^*. \tag{820, 14}$$

The coefficients $g(N_A, N_B, N_{AB})$ are, however, not expressible in a simple form, and so we cannot evaluate either $\Xi$ or $\Xi_{(N^*)}$ by any direct method. We therefore use the device described in § 608.

We define $N$, $\xi$, $\eta$, $\gamma$ by

$$N = N_A^* + N_B^*, \tag{820, 15}$$

$$\xi^N = \xi_A^{N_A^*} \xi_B^{N_B^*}, \tag{820, 16}$$

$$\eta^{\frac{1}{2}zN} = \eta_{AB}^{N_{AB}^*}, \tag{820, 17}$$

$$\gamma^N = g(N_A^*, N_B^*, N_{AB}^*). \tag{820, 18}$$

Thus $\xi$ and $\gamma$ are the geometric mean contributions per molecule, whether $A$ or $B$, to the factor $\xi_A^{N_A^*} \xi_B^{N_B^*}$ and to the factor $g(N_A^*, N_B^*, N_{AB}^*)$ in $\Xi_{(N^*)}$ respectively; $\eta$ is the geometric mean contribution of each pair of neighbours to the factor $\eta_{AB}^{N_{AB}^*}$ in $\Xi_{(N^*)}$. We can then write

$$\Xi_{(N^*)} = \gamma^N \xi^N \eta^{\frac{1}{2}zN}. \tag{820, 19}$$

Finally we denote by $\eta_A$ the geometric mean contribution of a pair of neighbours, of which the first is specified to be an $A$, to the factor $\eta_{AB}^{N_{AB}^*}$ in $\Xi_{(N^*)}$; we define $\eta_B$ similarly.

From these definitions we can write down various alternative expressions equal in magnitude to $\Xi$; this involves an approximation the nature of which

was discussed in § 609. In particular we have the two following

$$\Xi_1 = (\xi_A \eta_A^z + \xi_B \eta_B^z)\gamma^{N-1}\xi^{N-1}\eta^{\frac{1}{2}zN-z}; \qquad (820, 20)$$

$$\Xi_2 = \{(\xi_A \eta_A^{z-1})^2 + 2\xi_A \eta_A^{z-1}\xi_B \eta_B^{z-1}\eta_{AB} + (\xi_B \eta_B^{z-1})^2\}\gamma^{N-2}\xi^{N-2}\eta^{\frac{1}{2}zN-2z+1}. \qquad (820, 21)$$

The form $\Xi_1$ corresponds to regarding the assembly as a central molecule, whether $A$ or $B$, in a field due to the remaining molecules; the form $\Xi_2$ corresponds to regarding the assembly as a molecular pair, of specified position but unspecified type, in a field due to the remaining molecules. In the first factor in (20) the first term is the contribution when the central molecule is an $A$, and the second is the contribution when it is a $B$. Hence the ratio of the frequencies of this molecule being an $A$ or $B$, which is equal to the ratio of the average number of molecules of the type $A$ and $B$ in the assembly, is given by

$$\frac{\overline{N_A}}{\overline{N_B}} = \frac{\xi_A \eta_A^z}{\xi_B \eta_B^z}. \qquad (820, 22)$$

In the first factor in (21) the three terms are the contributions of an $AA$ pair, an $AB$ (or $BA$) pair, and a $BB$ pair respectively. Hence the ratios of $\overline{N_{AB}}$, the average number of $AB$ pairs, to $\overline{N_{AA}}$, the average number of $AA$ pairs, and to $\overline{N_{BB}}$, the average number of $BB$ pairs, are given by

$$\frac{\overline{N_{AA}}}{(\xi_A \eta_A^{z-1})^2} = \frac{\overline{N_{AB}}}{2\xi_A \eta_A^{z-1}\xi_B \eta_B^{z-1}\eta_{AB}} = \frac{\overline{N_{BB}}}{(\xi_B \eta_B^{z-1})^2}. \qquad (820, 23)$$

Since $\overline{N_{AA}} = \frac{1}{2}(z\overline{N_A} - \overline{N_{AB}})$, $\overline{N_{BB}} = \frac{1}{2}(z\overline{N_B} - \overline{N_{AB}})$, these ratios can be put in the form

$$\frac{z\overline{N_A} - \overline{N_{AB}}}{(\xi_A \eta_A^{z-1})^2} = \frac{\overline{N_{AB}}}{\xi_A \eta_A^{z-1}\xi_B \eta_B^{z-1}\eta_{AB}} = \frac{z\overline{N_B} - \overline{N_{AB}}}{(\xi_B \eta_B^{z-1})^2}. \qquad (820, 24)$$

We can eliminate $\xi_A \eta_A^{z-1}/\xi_B \eta_B^{z-1}$ from the two equations (24) and obtain

$$\overline{N_{AB}}^2 = (z\overline{N_A} - \overline{N_{AB}})(z\overline{N_B} - \overline{N_{AB}})\eta_{AB}^2. \qquad (820, 25)$$

Replacing $\overline{N_{AB}}$ by $z\overline{X}$ and $\eta_{AB}$ by its value given by (8), we obtain

$$\overline{X}^2 = (\overline{N_A} - \overline{X})(\overline{N_B} - \overline{X})e^{-2w_{AB}/zkT}, \qquad (820, 26)$$

which is the relation we had to prove.

In deriving (26) we have made no use of (22), nor have we needed to evaluate the unknown quantities $\eta_A$ or $\eta_B$. If, however, we could evaluate the ratio $\eta_A/\eta_B$, then by substitution into (22) we should obtain directly the equilibrium value of the ratio $N_A/N_B$ for given $\lambda_A$, $\lambda_B$, without requiring to construct the free energy as was done in the previous section. We can as a

matter of fact determine the ratio $\eta_A/\eta_B$ as follows. If we eliminate $\overline{N_{AB}}$, instead of $\xi_A \eta_A^{z-1}/\xi_B \eta_B^{z-1}$, from the two equations (24), we obtain

$$\frac{\overline{N_A}}{\overline{N_B}} = \frac{\xi_A \eta_A^{z-1}(\xi_A \eta_A^{z-1} + \xi_B \eta_B^{z-1} \eta_{AB})}{\xi_B \eta_B^{z-1}(\xi_A \eta_A^{z-1} \eta_{AB} + \xi_B \eta_B^{z-1})}. \qquad (820, 27)$$

If we denote $(\eta_A/\eta_B)^{z-1}$ by $\rho$, and omit the average signs on $\overline{N_A}$ and $\overline{N_B}$ which are no longer necessary, then (22) and (27) give us

$$\frac{N_A}{N_B} = \frac{\xi_A}{\xi_B} \rho^{z/(z-1)}, \qquad (820, 28)$$

$$\frac{N_A}{N_B} = \frac{\xi_A \rho(\xi_A \rho + \xi_B \eta_{AB})}{\xi_B(\xi_A \rho \eta_{AB} + \xi_B)}, \qquad (820, 29)$$

respectively. (29) is a quadratic equation in $\xi_A \rho/\xi_B$ with the positive root

$$\frac{\xi_A \rho}{\xi_B} = \frac{(N_A - N_B)\eta_{AB} + \sqrt{(N_A - N_B)^2 \eta_{AB}^2 + 4N_A N_B}}{2N_B}. \qquad (820, 30)$$

Eliminating $\rho$ from (28) and (30), we obtain

$$\frac{\xi_A}{\xi_B} = \frac{N_A}{N_B} \left\{ \frac{(N_A - N_B)\eta_{AB} + \sqrt{(N_A - N_B)^2 \eta_{AB}^2 + 4N_A N_B}}{2N_A} \right\}^z. \qquad (820, 31)$$

Replacing $\xi_A$, $\xi_B$, $\eta_{AB}$ by their values given by (7) and (8), we obtain

$$\frac{\lambda_A \phi_A v_A e^{(\chi_A + kT)/kT}}{\lambda_B \phi_B v_B e^{(\chi_B + kT)/kT}} = \frac{N_A}{N_B} \left\{ \frac{(N_A - N_B) + \sqrt{(N_A - N_B)^2 + 4N_A N_B e^{2w_{AB}/zkT}}}{2N_A e^{w_{AB}/zkT}} \right\}^z. \qquad (820, 32)$$

We have thus obtained an explicit formula for the ratio of the absolute activities $\lambda_A/\lambda_B$, as a function of the molecular ratio $N_A/N_B$. To obtain the absolute values of $\lambda_A$ and $\lambda_B$ one would have to combine (32) with the thermodynamic relation

$$\frac{\partial \log \lambda_A}{\partial N_B} = \frac{\partial \log \lambda_B}{\partial N_A}. \qquad (820, 33)$$

There is, however, no simple explicit solution of the simultaneous equations (32) and (33) for $\lambda_A$, $\lambda_B$. The use of equation (26) as described in § 819 is therefore a more profitable procedure. We can, however, conveniently derive the critical mixing temperature from (32). The condition for internal stability of a phase* can be expressed in the form

$$\frac{\partial \log(\lambda_A/\lambda_B)}{\partial \log(N_A/N_B)} > 0. \qquad (820, 34)$$

* A complete discussion of stability conditions will be found for example in Schottky, *Thermodynamik*, Chapter F (Springer, 1929)

There will be splitting into two phases if the equation

$$\frac{\partial \log(\lambda_A/\lambda_B)}{\partial \log(N_A/N_B)} = 0 \qquad (820, 35)$$

has two real roots. Somewhere between these two roots there will be a real root of the equation

$$\frac{\partial^2 \log(\lambda_A/\lambda_B)}{\partial[\log(N_A/N_B)]^2} = 0. \qquad (820, 36)$$

The critical conditions occur when (35) and (36) are simultaneously satisfied. By substituting from (32) into (35) and (36), we obtain for the state of critical mixing

$$N_A/N_B = 1, \qquad (820, 37)$$

$$e^{-w_{AB}/zkT} = 1 - 2/z, \qquad (820, 38)$$

in agreement with (819, 22).

**§ 821. Molecules of markedly different size and shape.** We recall that all the formulae yet given in this chapter depend on the assumption that the two types of molecules can be treated as spheres of at least roughly the same size. From any given configuration of the assembly we can then obtain another distinct one by merely interchanging the positions of a pair of unlike molecules, without appreciably affecting the configuration of the remaining molecules. When this condition is not fulfilled, the problem of evaluating the factor $\Omega(T)$ in the partition function, which allows for the various configurations of the assembly, becomes almost prohibitively difficult, and until quite recently no progress had been made, even in obtaining a rough approximation.

Some progress has recently been made in the evaluation of $\Omega(T)$ for an assembly of two types of molecules, one twice the size of the other. The two types of molecule are supposed to differ in size in such a way that the larger has effectively the same size and shape as two of the smaller in close contact. The larger molecule can therefore be interchanged with any two smaller molecules, which are closest neighbours, in forming a new distinct configuration from an existing one. The two types of molecule are further assumed to be so similar chemically that the energy of mixing, analogous to the quantity $w_{AB}$ in §§ 814–820, is zero. This means that any deviations from the laws of perfect solutions are due entirely to the differences of size and shape of the two components. The resulting difference in the equilibrium properties of the mixture can most directly be expressed as a difference in the entropy of mixing defined in § 815.

For a perfect mixture of molecules $A$ and $B$, of at least approximately the same size, the number of distinguishable configurations is, as we have seen,

$$(N_A + N_B)!/N_A!\,N_B!, \qquad (821, 1)$$

and this expression occurs as a factor in $\Omega$. We may call this the combinatory factor in $\Omega$. We saw in § 815 that

$$\Delta S = k \log \frac{(N_A + N_B)!}{N_A!\, N_B!} = k\left\{N_A \log \frac{N_A + N_B}{N_A} + N_B \log \frac{N_A + N_B}{N_B}\right\}. \quad (821, 2)$$

The problem before us is to determine the number of distinguishable configurations of $N_A$ molecules $AA'$ and $N_B$ molecules $B$ when each $AA'$ molecule has the same size and shape as two $B$ molecules. If this number can be determined, it must be used instead of (1) as the combinatory factor in $\Omega(T)$. We shall then be able to construct the entropy of mixing, just as we constructed (2) from (1). A first attack on this problem was made by Fowler and Rushbrooke;* this can be carried further by using some new results by Chang.† The approximation is made that the liquid configurations are equivalent to those of a simple, regular lattice, the difference in size and shape being allowed for by requiring each $AA'$ molecule to occupy two neighbouring lattice points, while each $B$ molecule occupies one. The calculations thus apply strictly, so far as they go, to a mixed crystal, and only by inference to a liquid mixture.

By an application of a method, similar to that described in § 608 and involving an approximation analogous to that discussed in § 609, Chang has shown that for a mixture of $N_A$ double molecules‡ $AA'$ and $N_B$ single molecules $B$, having the properties described, the combinatory factor[A] must be replaced by

$$\left[\frac{\{2(z-1)\, N_A/z + N_B\}!}{(2N_A/z)!\,(2N_A + N_B)!}\right]^{\frac{1}{2}z} \frac{(2N_A + N_B)!}{N_B!}\left(\frac{2}{\sigma_{AA'}}\right)^{N_A}, \quad (821, 3)$$

where $z$ denotes the number of nearest neighbours of a lattice point and $\sigma_{AA'}$ is a symmetry number equal to 2 if the two ends of an $AA'$ molecule are indistinguishable and equal to 1 otherwise. The combinatory term in the entropy of the mixture is $k$ times the logarithm of the expression (3), that is to say

$$\begin{aligned} &k\,\tfrac{1}{2}z\{2(z-1)\, N_A/z + N_B\} \log\{2(z-1)\, N_A/z + N_B\} - k\,\tfrac{1}{2}z(2N_A/z)\log(2N_A/z) \\ &\quad - k\,\tfrac{1}{2}z(2N_A + N_B)\log(2N_A + N_B) + k(2N_A + N_B)\log(2N_A + N_B) \\ &\quad - kN_B \log N_B + kN_A \log(2/\sigma_{AA'}) \\ &= k\{(z-1)\, N_A + \tfrac{1}{2}zN_B\} \log \frac{2(z-1)\, N_A/z + N_B}{2N_A + N_B} - kN_A \log \frac{2N_A/z}{2N_A + N_B} \\ &\quad - kN_B \log \frac{N_B}{2N_A + N_B} + kN_A \log \frac{2}{\sigma_{AA'}}. \end{aligned} \quad (821, 4)$$

* Fowler and Rushbrooke, *Trans. Fara. Soc.* **33**, 1272 (1937).

† Chang, *Proc. Camb. Phil. Soc.* **35**, 265 (1939).

‡ It would be more logical to use the symbol $N_{AA'}$ but we use $N_A$ simply because it is unambiguous and occurs so often. We do not abbreviate $\sigma_{AA'}$, $\mu_{AA'}$ or $p_{AA'}$ as these occur in comparatively few places.

[A] See appendix, § A 8.

This expression reduces to zero for the pure liquid $B$, when we set $N_A = 0$; but when we set $N_B = 0$, we obtain as the combinatory term in the entropy of the pure liquid $AA'$

$$kN_A(z-1)\log\frac{z-1}{z} + kN_A\log z + kN_A\log\frac{2}{\sigma_{AA'}}, \qquad (821,5)$$

due to the distinguishable ways in which $N_A$ molecules $AA'$ can pack amongst themselves. If we subtract (5) from (4) we obtain for $\Delta S$ the entropy of mixing

$$\Delta S/k = \{(z-1)N_A + \tfrac{1}{2}zN_B\}\log\frac{2(z-1)N_A/z + N_B}{2N_A+N_B} - N_A\log\frac{2N_A/z}{2N_A+N_B}$$
$$- N_B\log\frac{N_B}{2N_A+N_B} - (z-1)N_A\log(z-1) + (z-2)N_A\log z, \quad (821,6)$$

whether or no the molecules $AA'$ be symmetrical.

The approximations leading to (6) can be controlled by the following comparisons. In the first place the results of (6) for either $N_A \ll N_B$ or $N_B \ll N_A$ can be compared with the results of the earlier calculations of Fowler and Rushbrooke, which were obtained by entirely different arguments and depend on approximations of a quite different type. The two methods, where both apply, give results in substantial agreement. Secondly one may note that in the special case of $z = 2$ the expression (6) for the entropy of mixing reduces to (2). This is as should be, since $z = 2$ corresponds to the arrangement of all the molecules in a linear chain, for this case the number of distinguishable arrangements must be independent of the relative lengths of the two types of molecules, and in particular must have the same value whether there are $N_A$ molecules $A$ of the same size as the $N_B$ molecules $B$, or there are $N_A$ molecules $AA'$ of double their length.

Since the energy of mixing $\Delta E$ and the volume change $\Delta V$ on mixing are by supposition zero, the free energy of mixing and the Gibbs function of mixing are given by

$$\Delta F = \Delta G = -T\Delta S. \qquad (821,7)$$

We can obtain the difference between the partial potential $\mu_{AA'}$ of $AA'$ in the mixture and its value $\mu^0_{AA'}$ for the pure substance at the same temperature and pressure by substituting from (6) into (7) and differentiating with respect to $N_A$. A similar procedure leads to $\mu_B - \mu^0_B$. We thus obtain

$$\mu_{AA'} = \mu^0_{AA'} + kT[-(z-1)\log\{N_A + \tfrac{1}{2}zN_B/(z-1)\}$$
$$+ \log N_A + (z-2)\log(N_A + \tfrac{1}{2}N_B)], \quad (821,8)$$

$$\mu_B = \mu^0_B + kT[-\tfrac{1}{2}z\log\{N_B + 2(z-1)N_A/z\} + \log N_B + (\tfrac{1}{2}z-1)\log(N_B+2N_A)]. \quad (821,9)$$

It follows as in § 816, for the partial vapour pressures, that

$$\frac{p_{AA'}}{p^0_{AA'}} = \frac{N_A(N_A+\frac{1}{2}N_B)^{z-2}}{\{N_A+\frac{1}{2}zN_B/(z-1)\}^{z-1}}, \tag{821, 10}$$

$$\frac{p_B}{p^0_B} = \frac{N_B(N_B+2N_A)^{\frac{1}{2}(z-2)}}{\{N_B+2(z-1)\,N_A/z\}^{\frac{1}{2}z}}. \tag{821, 11}$$

All these formulae, as we have already stated for formula (6), reduce to the formulae for perfect solutions when $z = 2$. For all larger values of $z$ there is a deviation from the linear variation of $p_{AA'}$ and $p_B$ with molecular fraction typical of perfect solutions. The nature of this deviation is illustrated by Table 9, in which calculated values are given for the ratio of the actual vapour pressures to those calculated according to Raoult's law. The calculations have been made for $z = 8$ corresponding to body-centred cubic packing, for $z = 12$ corresponding to closest packing, and also for $z = \infty$. In the last case formulae (10) and (11) take the limiting forms

$$\frac{p_{AA'}}{p^0_{AA'}} = \frac{2N_A}{2N_A+N_B}\,e^{-N_B/(2N_A+N_B)}, \tag{821, 12}$$

$$\frac{p_B}{p^0_B} = \frac{N_B}{2N_A+N_B}\,e^{N_A/(2N_A+N_B)}. \tag{821, 13}$$

TABLE 9

*Deviations of partial vapour pressures from values for perfect solutions when the molecules AA′ are twice the size of the molecules B*

$N_A$, $N_B$ denote numbers of molecules of two kinds and $p_{AA'}$, $p_B$ their partial vapour pressures. $z$ is the number of nearest neighbours of a molecule $B$ or a half molecule $A$.

| $N_A/(N_A+N_B)$ | $\frac{p_{AA'}}{p^0_{AA'}}\frac{N_A+N_B}{N_A}$ | | | $\frac{p_B}{p^0_B}\frac{N_A+N_B}{N_B}$ | | |
|---|---|---|---|---|---|---|
| | $z = 8$ | $z = 12$ | $z = \infty$ | $z = 8$ | $z = 12$ | $z = \infty$ |
| 0·0 | 0·785 | 0·768 | 0·736 | 1·000 | 1·000 | 1·000 |
| 0·1 | 0·839 | 0·824 | 0·803 | 0·997 | 0·996 | 0·995 |
| 0·2 | 0·882 | 0·871 | 0·855 | 0·988 | 0·986 | 0·984 |
| 0·3 | 0·916 | 0·908 | 0·895 | 0·976 | 0·973 | 0·969 |
| 0·4 | 0·943 | 0·938 | 0·932 | 0·959 | 0·957 | 0·951 |
| 0·5 | 0·963 | 0·962 | 0·955 | 0·944 | 0·940 | 0·930 |
| 0·6 | 0·977 | 0·975 | 0·974 | 0·926 | 0·920 | 0·909 |
| 0·7 | 0·988 | 0·986 | 0·985 | 0·909 | 0·901 | 0·887 |
| 0·8 | 0·996 | 0·993 | 0·994 | 0·890 | 0·881 | 0·866 |
| 0·9 | 0·998 | 0·998 | 0·998 | 0·871 | 0·862 | 0·845 |
| 1·0 | 1·000 | 1·000 | 1·000 | 0·853 | 0·843 | 0·824 |

Though the theory is still very rough, one may safely conclude that deviations from the laws of perfect solutions should exist for mixtures of molecules of different sizes, even in the absence of any energy of mixing.

The only other useful discussion of a mixture of molecules of greatly different sizes is due to Hildebrand.* He considers a mixture of long rod-shaped molecules of equal cross-sections but different lengths and assumes that in the liquid phase they must pack parallel to one another as in a crystal. As we have already mentioned, the number of ways of arranging two kinds of molecules in a single line is independent of their relative lengths. If then a liquid is constructed out of large groups of such lines all parallel to one another, it seems not unreasonable to expect the entropy of mixing to be nearly the same as for a single linear array, that is to say the same as for a mixture of spherical molecules all the same size. Hildebrand suggests that this may be the case for a mixture of two paraffins having molecules of greatly differing lengths and that Raoult's law should be obeyed. It has been shown quite recently† that Raoult's law is in fact obeyed with high accuracy by mixtures of $C_6H_{14}$ (hexane) and $C_{16}H_{34}$ (hexadecane) throughout the whole range of composition.

With the available experimental data it is difficult, if not impossible, to separate the effects of an energy of mixing, $w_{AB}$, from the effects of a molecular volume ratio differing greatly from unity. The best hope of separating these probably lies in determining the complete curves of partial vapour pressures against composition over as wide a range of temperatures as possible. For the effect of $w_{AB}$ differing from zero gives, according to the first crude approximation, a contribution to $F$ independent of the temperature, while the volume ratio effect gives a contribution to $S$ approximately independent of temperature. The corresponding contributions to $\log p$ are inversely proportional to $T$, and independent of $T$, respectively.

**§ 822. Ideal dilute solutions.** We now return to regular solutions and shall investigate the properties of such solutions, when one species, say $A$, called the solvent, is present in large excess compared with the other dilute species $B$ called the solute. For such solutions, called ideal dilute solutions, the formulae for regular solutions simplify appreciably. The free energy of a binary regular solution is given by (817, 3) with $\bar{\bar{X}}$ related to $\bar{X}$ by (817, 10), and $\bar{X}$ in turn given by (819, 4). We now assume that $N_B \ll N_A$ so that $(N_B/N_A)^2$ may be neglected. We may then replace the right side of (819, 4) by its leading term, and so have

$$\bar{X} \sim \frac{N_A N_B}{N_A + N_B} \sim N_B; \qquad (822, 1)$$

* Hildebrand, *J. Am. Chem. Soc.* **59**, 794 (1937).

† Hildebrand and Sweny, *J. Phys. Chem.* **43**, 297 (1939).

consequently according to (817, 10) with sufficient accuracy

$$\bar{\bar{X}} = \bar{X} = N_B. \tag{822, 2}$$

The physical meaning of (2) is simple: there are so few $B$ molecules present compared with $A$ molecules that practically every $B$ molecule is entirely surrounded by $A$ molecules and there are practically no $BB$ pairs of close neighbours. In other words, the solution is so dilute that mutual interactions between solute molecules are negligible. This condition is fulfilled only in the absence of long-range forces between solute particles, and is not fulfilled in a solution of an electrolyte where the solute particles are electrically charged ions. Solutions of electrolytes will be discussed in the next chapter, where we shall see that, even at the highest dilutions attainable in practice, the properties of such solutions deviate appreciably from those of ideal solutions.

Substituting the value of $\bar{\bar{X}}$ given by (2) into (817, 3) and ignoring, as usual, the difference in value between $F$ and $G$, which is negligible at ordinary pressures, we obtain

$$\begin{aligned} G \simeq F = N_A\left\{-\chi_A - kT\log(\phi_A v_A) - kT + kT\log\frac{N_A}{N_A+N_B}\right\} \\ + N_B\left\{-\chi_B + w_{AB} - kT\log(\phi_B v_B) - kT + kT\log\frac{N_B}{N_A+N_B}\right\}. \end{aligned} \tag{822, 3}$$

This formula is readily extended to a solution with more than one dilute (solute) species. If we denote the solvent species by $l$ and the several solute species by $s$, we have

$$\begin{aligned} G \simeq F = N_l\left\{-\chi_l - kT\log(\phi_l v_l) - kT + kT\log\frac{N_l}{N_l+\Sigma_s N_s}\right\} \\ + \Sigma_s N_s\left\{-\chi_s + w_{ls} - kT\log(\phi_s v_s) - kT + kT\log\frac{N_s}{N_l+\Sigma_s N_s}\right\}. \end{aligned} \tag{822, 4}$$

For the partial potentials $\mu_l$ of the solvent and $\mu_s$ of the solute species we derive

$$\mu_l = \frac{\partial G}{\partial N_l} = -\chi_l - kT\log(\phi_l v_l) - kT + kT\log\frac{N_l}{N_l+\Sigma_s N_s}, \tag{822, 5}$$

$$\mu_s = \frac{\partial G}{\partial N_s} = -\chi_s + w_{ls} - kT\log(\phi_s v_s) - kT + kT\log\frac{N_s}{N_l+\Sigma_s N_s}. \tag{822, 6}$$

We obtain the partial vapour pressures as usual by equating the partial potentials in the liquid and gas phases. We thus obtain

$$p_l = \frac{kT\phi_l^G}{v_l\phi_l^L} e^{-(\chi_l+kT)/kT} \frac{N_l}{N_l+\Sigma_s N_s}, \tag{822, 7}$$

$$p_s = \frac{kT\phi_s^G}{v_s\phi_s^L} e^{-(\chi_s-w_{ls}+kT)/kT} \frac{N_s}{N_l+\Sigma_s N_s}. \tag{822, 8}$$

If we compare these formulae for the partial vapour pressures $p_l$, $p_s$ of the solution with those for the vapour pressures $p_l^0$, $p_s^0$ of the pure liquids, we find

$$p_l = p_l^0 \frac{N_l}{N_l + \Sigma_s N_s}, \tag{822, 9}$$

$$p_s = p_s^0 e^{w_{ls}/kT} \frac{N_s}{N_l + \Sigma_s N_s}. \tag{822, 10}$$

Formula (9) for the solvent is of exactly the same form as formulae (816, 2) for perfect solutions and is Raoult's law. Formula (10) on the other hand differs from Raoult's law by the extra factor $e^{w_{ls}/kT}$ and expresses Henry's law. We can loosely describe the product $p_s^0 e^{w_{ls}/kT}$ as the idealized vapour pressure of the species $s$ at a molecular fraction unity if the environment of the molecules were the same as in a dilute solution in the solvent $l$. We can abbreviate (10) to

$$p_s = k_{ls} \frac{N_s}{N_l + \Sigma_s N_s}, \tag{822, 11}$$

where the coefficient $k_{ls}$ depends on the nature of the solvent $l$ and of the solute $s$ but is independent of the concentrations of any of the solute species.

§ 823. **Extended theory of ideal dilute solutions.** We have derived the properties of ideal dilute solutions by regarding them as a special class of regular solutions. Actually the laws of ideal dilute solutions are more general, being independent of the assumption that all the molecules have comparable volumes and similar manners of packing. We shall therefore give an alternative derivation of these laws, starting with a different method of approximation.

In the absence of long-range forces (i.e. for non-electrolytes) and for sufficiently high dilutions we may ignore interactions between two or more solute molecules. We therefore start with the assumption of treating the assembly of solute molecules as a perfect quasi-gas of molecules moving freely in a region of volume $V$ in which the solute molecules of types $s$ have a constant potential energy $-\chi_{ls}$, which may depend on $T$; as usual we take the state of infinite separation as energy zero. For any given configuration of the solute molecules there will be a volume $V - \Sigma_s N_s V_s$ available for the $N_l$ solvent molecules, of a shape depending on the configuration. We may reasonably, and shall, assume that the thermodynamic properties of the solvent in this volume are independent of the volume's shape. On these assumptions the assembly will have a free energy given by

$$F = F_l(T, V - \Sigma_s N_s V_s, N_l) + \Sigma_s N_s \left\{ -\chi_{ls} - kT \log \frac{(2\pi m_s kT)^{\frac{3}{2}} V}{h^3} - kT \log j_s(T) - kT + kT \log N_s \right\}, \tag{823, 1}$$

when we use the standard contributions for the solute species characteristic of an ideal gas mixture in a volume $V$. We then find from (1)

$$\mu_s = -\chi_{ls} - kT\log\frac{(2\pi m_s kT)^{\frac{3}{2}}}{h^3} - kT\log j_s(T) + kT\log\frac{N_s}{V} - V_s\frac{\partial F_l}{\partial V}. \tag{823, 2}$$

But on our assumptions $-\partial F_l/\partial V$ is the pressure $P$ at which the pure solvent has the volume $V - \Sigma_s N_s V_s$, and this will not differ appreciably from the pressure on the actual assembly. We may also simplify $\mu_s$ by using the notation $\phi_s(T)$ defined in (813, 2). We thus find

$$\mu_s = -\chi_{ls} + PV_s - kT\log\phi_s(T) + kT\log\frac{N_s}{V}. \tag{823, 3}$$

From the unsymmetrical nature of our approximations, which treat the solvent as a medium in which the solute molecules are immersed, we shall not expect to be able to derive a reliable value for $\mu_l$.

Equation (2) represents the most accurate result to which our assumptions lead. It can, however, be simplified in various ways. In the first place $PV_s$ is as usual negligible for all ordinary values of the pressure and may be omitted. Secondly, $V$ is related to the molecular volumes by the equation $V = N_l V_l + \Sigma_s N_s V_s$. Since $N_s \ll N_l$ and usually $V_l \simeq V_s$, we may put

$$V = (N_l + \Sigma_s N_s) V_l. \tag{823, 4}$$

Making these further approximations, we have

$$\mu_s = -\chi_{ls} - kT\log(\phi_s V_l) + kT\log\frac{N_s}{N_l + \Sigma_s N_s}. \tag{823, 5}$$

We observe that (5) is formally equivalent to (822, 6) if we assign to $\chi_{ls}$ the value

$$\chi_{ls} = \chi_s - w_{ls} + kT + kT\log\frac{v_s}{V_l}. \tag{823, 6}$$

We obtain the vapour pressure as usual by equating the partial potentials in the liquid and gas phases. We may with equal accuracy use either (2) or (5) for the partial potential in the solution. We thus find

$$p_s \propto \frac{N_s}{V} \propto \frac{N_s}{N_l + \Sigma_s N_s}, \tag{823, 7}$$

which is Henry's law.

We have already mentioned that the present model cannot give the equilibrium properties of the solvent. But we can deduce the dependence of $\mu_l$ on the composition by using the thermodynamic relation

$$N_l d\mu_l + \Sigma_s N_s d\mu_s = 0 \quad (T, P \text{ constant}), \tag{823, 8}$$

known as the Gibbs-Duhem relation. To use this it is simplest to introduce the molecular fractions $x_l$, $x_s$ defined by

$$x_l = \frac{N_l}{N_l + \Sigma_s N_s}, \quad x_s = \frac{N_s}{N_l + \Sigma_s N_s}. \tag{823, 9}$$

If we divide (8) by $(N_l + \Sigma_s N_s)$, we obtain

$$x_l d\mu_l + \Sigma_s x_s d\mu_s = 0 \quad (T, P \text{ constant}), \tag{823, 10}$$

and from (5) we have

$$d\mu_s = kTd \log x_s \quad (T, P \text{ constant}). \tag{823, 11}$$

Substituting (11) into (10), we obtain

$$d\mu_l = -\frac{kT}{x_l} \Sigma_s x_s d \log x_s = -\frac{kT}{x_l} \Sigma_s dx_s. \tag{823, 12}$$

But by the definitions of $x_l$, $x_s$ we have the identity

$$dx_l + \Sigma_s dx_s \equiv 0, \tag{823, 13}$$

and so according to (12)

$$d\mu_l = \frac{kT}{x_l} dx_l = kTd \log x_l. \tag{823, 14}$$

Finally integrating (14), we obtain

$$\begin{aligned} \mu_l &= \mu_l^0 + kT \log x_l \\ &= \mu_l^0 + kT \log \frac{N_l}{N_l + \Sigma_s N_s}, \end{aligned} \tag{823, 15}$$

where $\mu_l^0$ is independent of $N_l$, $N_s$. From (15) we can immediately deduce Raoult's law in the form

$$p_l = p_l^0 \frac{N_l}{N_l + \Sigma_s N_s}, \tag{823, 16}$$

without requiring to know the form of $\mu_l^0$.

Having obtained the forms of the partial potentials for ideal dilute solutions, we can deduce all the equilibrium properties by ordinary thermodynamic reasoning.* We shall here content ourselves with two important examples.

§ 824. **Heat of dilution.** By definition an ideal solution is one in which the interaction between solute molecules is negligible. Any two such solutions therefore, having the same solvent, temperature and pressure, will mix without absorption or evolution of heat. This may be rigorously established by a thermodynamic calculation, since in *any* process at con-

* See, for example, *M.T.* Chapter VI.

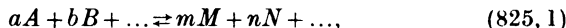
stant temperature and pressure, involving no work other than that done by the pressure, the increase in the heat content $H$ is equal to the heat taken in. The partial molecular heat contents $H_l$, $H_s$ are related to the partial potentials by the thermodynamic formulae

$$H_l = -T^2\left(\frac{\partial[\mu_l/T]}{\partial T}\right)_{P,N_l,N_s}. \qquad (824, 1)$$

$$H_s = -T^2\left(\frac{\partial[\mu_s/T]}{\partial T}\right)_{P,N_l,N_s}. \qquad (824, 2)$$

When we substitute for $\mu_l$, $\mu_s$ whether from (822, 5), (822, 6) or from (823, 15), (823, 5) into (1), (2) respectively, we find that $H_l$, $H_s$ are for given $T$, $P$ and solvent independent of $N_l$, $N_s$. Any two ideal solutions having a common solvent will therefore mix at constant temperature and pressure without absorption or evolution of heat. In particular this applies to the mixing of one such solution with pure solvent. In other words, the heat of (further) dilution of an ideal solution is zero.

§ 825. **Homogeneous chemical equilibria.** If we write the general chemical reaction as

$$aA + bB + \ldots \rightleftarrows mM + nN + \ldots, \qquad (825, 1)$$

or

$$\Sigma_A aA \rightleftarrows \Sigma_M mM, \qquad (825, 2)$$

the condition for equilibrium is

$$\Sigma_A a\mu_A = \Sigma_M m\mu_M. \qquad (825, 3)$$

If the chemical species involved are all solute species in an ideal solution in a common solvent, each partial potential will according to (823, 5) be of the form

$$\mu_s = \mu_{ls}^0 + kT \log x_s, \qquad (825, 4)$$

where $\mu_{ls}^0$ depends on the temperature and the nature of the solvent $l$ and the solute $s$ but is independent of the concentrations, and $x_s$ denotes the molecular fraction $N_s/(N_l + \Sigma_s N_s)$. When we substitute from (4) into (3) we obtain

$$\Sigma_M m \log x_M - \Sigma_A a \log x_A = (\Sigma_A a\mu_A^0 - \Sigma_M m\mu_M^0)/kT. \qquad (825,5)$$

This can be written as

$$\frac{(x_M)^m (x_N)^n \ldots}{(x_A)^a (x_B)^b \ldots} = K_x, \qquad (825, 6)$$

where $K_x$ depends on the temperature and on the solvent but not on the solute concentrations. This is the law of mass action for ideal solutions.

If we denote the concentration of solute molecules per unit volume by $c_s$, we have at high dilutions the approximation

$$c_s = \frac{N_s}{N_l V_l + \Sigma_s N_s V_s} \sim \frac{N_s}{(N_l + \Sigma_s N_s) V_l} = \frac{x_s}{V_l}. \qquad (825,7)$$

We may therefore replace (6) by the alternative form of the law of mass action

$$\frac{(c_M)^m (c_N)^n \dots}{(c_A)^a (c_B)^b \dots} = K_c, \qquad (825,8)$$

where
$$K_c = K_x (V_l)^{(a+b+\dots-m-n-\dots)}, \qquad (825,9)$$

and $K_c$, like $K_x$, is independent of the solute concentrations.

Footnote to p 344

The ratio $T_m/T_c$ of the melting-point $T_m$ to the critical temperature $T_c$ should also have the same value for different substances to which the law of corresponding states is applicable Actually $T_m/T_c$ lies between 0 548 and 0 557 for the four inert elements Ne, A, Kr, Xe, a remarkable verification of the law.

See Clusius and Weigand, *Zeit. Physikal. Chem.* B, **42**, 111 (1939).

# CHAPTER IX

## SOLUTIONS OF ELECTROLYTES

**§ 900. Strong electrolytes.** When certain substances such as common salt are dissolved in water, the solution has a comparatively high conductivity, showing that charged ions must be present, and the effect of the solute on the colligative properties of the dilute solution (vapour pressure of solvent, freezing-point, osmotic pressure) is always larger than that predicted by the laws of ideal solutions, assuming that the solute is present mainly as molecules of NaCl. We owe to Arrhenius the suggestion that for such substances, called *strong electrolytes*, the solute is composed largely of the independent systems $Na^+$ and $Cl^-$. Study of the optical properties of such solutions also leads to the conclusion that at least in dilute and moderately concentrated solutions there are at most very few NaCl molecules, and in many cases the properties of the solution can be accurately accounted for on the assumption that no undissociated molecules at all are present.*

**§ 901. Degree of dissociation.** It is of interest to examine whether this complete dissociation of salts is to be expected theoretically.† In the vapour state the calculation of the equilibrium

$$\mathrm{NaCl} \rightleftarrows \mathrm{Na}^+ + \mathrm{Cl}^- \qquad (901, 1)$$

is straightforward. We obtain, according to the formulae of Chapter v,

$$\frac{N_{\mathrm{Na}^+} N_{\mathrm{Cl}^-}}{V N_{\mathrm{NaCl}}} = \left(\frac{2\pi m_{\mathrm{Na}^+} m_{\mathrm{Cl}^-} kT}{m_{\mathrm{NaCl}} h^2}\right)^{\frac{3}{2}} \frac{h^2}{8\pi^2 A_{\mathrm{NaCl}} kT} \frac{1}{q(T)} e^{-\chi/kT}, \qquad (901, 2)$$

where $q(T)$ is the vibrational partition function for NaCl, and $\chi$ is the excess energy of a pair of free $Na^+$ and $Cl^-$ ions at rest over one NaCl molecule at rest in its lowest vibrational state. The value of $q(T)$ lies between 1 at low temperatures and $kT/h\nu$ at high, $\nu$ being the vibration frequency of the molecule, and can be taken as unity with sufficient accuracy for the present purpose. If $a$ is the distance apart of $Na^+$ and $Cl^-$ in the molecule, then the moment of inertia $A_{\mathrm{NaCl}}$ of the NaCl molecule is given by

$$A_{\mathrm{NaCl}} = \frac{m_{\mathrm{Na}^+} m_{\mathrm{Cl}^-} a^2}{m_{\mathrm{NaCl}}}. \qquad (901, 3)$$

We therefore have

$$\frac{N_{\mathrm{Na}^+} N_{\mathrm{Cl}^-}}{V N_{\mathrm{NaCl}}} = \left(\frac{2\pi m_{\mathrm{Na}^+} m_{\mathrm{Cl}^-} kT}{m_{\mathrm{NaCl}} h^2}\right)^{\frac{1}{2}} \frac{e^{-\chi/kT}}{4\pi a^2}. \qquad (901, 4)$$

* Bjerrum, *Proc. 7th Int. Cong. Pure and Applied Chem.* Sect. 10, p. 58 (London, 1909); *Zeit. Elektrochem.* **24**, 321 (1918).

† Cf. Guggenheim, *Report of Chem. Sect. Brit. Ass., Centenary Meeting*, 58 (1931).

The interaction energy of $Na^+$ and $Cl^-$ can be determined from the properties of NaCl crystals. According to Buckingham* the mutual potential energy of $Na^+$ and $Cl^-$ a distance $r$ cm. apart may be represented with very fair accuracy by the formula

$$-\frac{|e|^2}{r}+\frac{0\cdot280}{10^8(10^8r)^9}+\frac{4\cdot26\times10^{-3}}{10^8(10^8r)^6}; \qquad (901,5)$$

we obtain $a$ as the value of $r$ which makes the expression (5) a minimum, and thus find $a = 2\cdot37\times10^{-8}$ cm. We then obtain the value of $-\chi$ by substituting this value for $r$ into (5); we find $\chi = 8\cdot63\times10^{-12}$ ergs or $\chi/k = 6\cdot30\times10^4$ deg. Using these values and expressing the equilibrium concentrations $c$ in gram-ions (or gram-molecules) per litre,† we obtain for the equilibrium at 300° K.

$$K^{\text{Gas}} = \frac{c_{\text{Na}}\,c_{\text{Cl}^-}}{c_{\text{NaCl}}} = 10^2 e^{-\chi/kT}$$

$$\simeq 10^2 e^{-210} \simeq 10^{-89}. \qquad (901,6)$$

Thus *in the vapour* NaCl is, naturally, completely undissociated.

We must now introduce modifications due to the solvent, which in this chapter is almost always water, and for convenience will be spoken of as such. If we continue to regard the free ions as free systems not specifically associated with any water (solvent) molecules, that is as unhydrated (unsolvated), we have yet to remember that the energy of dissociation in water (the solvent) will be less than $\chi$. If we regard the water (solvent) merely as a continuous medium with dielectric constant $D$, the energy of separation of the pair of ions would be reduced to (roughly) $\chi/D$. We thus obtain in water with $D \simeq 80$

$$K_{\text{NaCl}} = \frac{c_{\text{Na}}\,c_{\text{Cl}}}{c_{\text{NaCl}}} \sim 10^2 e^{-2\cdot6} \sim 7. \qquad (901,7)$$

Similar calculations can be made for other ion pairs, for example $Na^+$ and $ClO_4^-$. In this case the rotational partition function of $ClO_4^-$ will not differ greatly from that of $NaClO_4$, except for the symmetry number, and we may with a sufficient accuracy assume this ratio to be given by the ratio of the symmetry numbers which we take to be 12 and 3 respectively. The equilibrium condition thus reduces to

$$\frac{N_{\text{Na}^+}N_{\text{ClO}_4^-}}{VN_{\text{NaClO}_4}} = \left(\frac{2\pi m_{\text{Na}^+}m_{\text{ClO}_4^-}kT}{m_{\text{NaClO}_4}h^2}\right)^{\frac{3}{2}} \tfrac{3}{12} e^{-\chi/kT}, \qquad (901,8)$$

instead of (4). If we take a reasonable value for $\chi$ *in vacuo* and use this value

* See *S.M.* Chapter x, p. 326.

† In this chapter we shall use the symbols $\nu$ to denote ions or molecules per cm.³ and $c$ to denote gram-ions or gram-molecules per litre. Thus $c = 1000\nu/\mathbf{N}$.

divided by 80 in water, we obtain in water

$$K_{NaClO_4} = \frac{c_{Na^+} c_{ClO_4^-}}{c_{NaClO_4}} \simeq 10^4. \qquad (901,9)$$

The much greater calculated value of $K$ for $NaClO_4$ as compared with that for NaCl arises from the great number of rotational states of $ClO_4^-$, which do not occur for the monatomic $Cl^-$. Similar rough estimates would lead to

$$K_{N(CH_3)_4Cl} \simeq 10^4; \qquad (901,10)$$

$$K_{N(CH_3)_4NO_3} \simeq 10^8. \qquad (901,11)$$

The above procedure for estimating $\chi$ in a solvent by dividing the value *in vacuo* by $D$ certainly overestimates the correction for a molecular solvent. In the very strong fields near an ion a saturation effect sets in, which will reduce considerably the effective value of $D$. The correct value of $K$ for NaCl must be very much less than seven in the absence of hydration, and a considerable degree of incompleteness in the dissociation is predicted for ordinary concentrations, in distinct disagreement with the actual facts. The error can only have entered by ignoring *hydration*, the intimate effect of the solvent molecules on the free ions.

We shall not here attempt any detailed analysis of the effect of hydration,* since in the present state of our knowledge it is difficult to reach any quantitative conclusions. Qualitatively there are two effects of hydration both favouring dissociation into ions. The first is that hydration of the ion is associated with a decrease of energy and this will decrease the effective $\chi$. The other effect is that the number of possible states of motion of the hydrated ion will be much greater than for a monatomic ion. In the comparison of NaCl and $NaClO_4$ we saw how polyatomic ions are favoured as compared with monatomic. Hydrated ions being polyatomic will also be favoured, though in a more complicated way, because the solvent molecules are involved in the equilibrium. These two effects together must be responsible for the complete or almost complete dissociation of salts of the type NaCl. Hydration is still more necessary to account for the almost complete dissociation of salts of the type $BaCl_2$, $LaCl_3$. On the other hand, hydration may not be necessary to explain the complete dissociation of salts such as $NaClO_4$ and $N(CH_3)_4Cl$ which yield at least one polyatomic ion.

**§ 902. Generalities concerning hydration of ions.** We have seen in the preceding section that in order that a salt composed of two monatomic ions may be highly dissociated its ions must be intimately associated with at least one water molecule, and therefore in this general sense hydrated. To

* For such an analysis see *S.M.* p. 539.

*form a more precise picture of hydration, and in particular to determine it quantitatively, various methods have been used. Methods based on the transport of water by ions in non-aqueous solvents are really irrelevant, as then the water is held by the ion against the attraction of the molecules of the less polar solvent, not against the attraction of other water molecules. The number of attached water molecules per ion thus comes out too high.* Methods based on mobilities in aqueous solution assume that the validity of Stokes' law for the terminal velocity of a sphere in a viscous liquid extends much further than can be justified. A simpler and theoretically sounder method is provided by a study of the densities of ionic solutions. In sufficiently dilute solution the partial molar volumes become constant and additive. They can be determined experimentally.

Now it is clear* from a variety of evidence that water has an irregular 4-coordinated structure, of open type, very similar to the regular 4-coordinated structure of ice. Each water molecule is generally surrounded by four others arranged more or less at the corners of a regular tetrahedron. On the other hand, when $H_2O$ molecules occur coordinated round ions in crystals they are closely packed round the ion and the number of $H_2O$ molecules coordinated to a given ion is just that number for which room is allowed by the relative sizes of the ion and the water molecule. Suppose now that an ion is introduced into liquid water. If it has a sufficient attraction for $H_2O$ molecules, it will cause some of these to pack tightly round it. The contraction associated with this packing can be calculated by comparing the volume occupied by each water molecule round the ion in a crystal with the molecular volume of pure water. In many cases this contraction is greater than the volume of the unhydrated ion, and the resulting partial ionic volume will then be negative.

A quantitative study of partial molar volumes shows that all monatomic positive ions, except the large $Rb^+$ and $Cs^+$, are completely hydrated in the sense that they are surrounded in water by a tightly packed layer of as many water molecules as their size allows, just as they are in crystals. The exceptions $Rb^+$ and $Cs^+$ appear to be so large that their surface field is insufficiently strong to coordinate the water. Monatomic negative ions are in general large, and except for $F^-$ appear to be unhydrated. Polyatomic negative ions are *a fortiori* unhydrated, while all multivalent monatomic ions are hydrated.

According to this deeper view of the structure of liquid water the theoretical computation of the degree of dissociation of a strong electrolyte becomes at present hopelessly complicated. The tentative calculations of the preceding section remain, however, sufficient to show that hydration is

* Bernal and Fowler, *J. Chem. Phys.* 1, 515 (1933).

an important factor in enhancing the dissociation for monatomic ions, especially multivalent ones. As the calculations of that section also show, such enhancement is not required for polyatomic ions and, as we see here, it probably does not occur for them.

**§ 903. The anomalies of strong electrolytes. The osmotic coefficient and the activity coefficients.** We have just seen that strong electrolytes, in water at least, are almost completely dissociated at low concentrations, certainly up to tenth molar. At such concentrations to regard the solute as completely dissociated into ions is at least as good an approximation as to assign any other constitution to it. It is therefore of great interest and importance to discuss theoretically the behaviour of solutions of such completely dissociated electrolytes at low concentrations —so low that the solutions would be ideal dilute in the sense of § 823 if it were not for the electrostatic interactions between the ions.

In an ideal aqueous solution the partial potential of the solvent water has the form

$$\mu_{H_2O} = \mu^0_{H_2O}(T, P) + kT \log x_{H_2O}, \qquad (903, 1)$$

where $x_{H_2O}$ denotes the molecular fraction of the water, and the superscript 0 the value for the pure liquid. If, on the other hand, the solution is not ideal, the deviation from ideality may be conveniently measured by a coefficient $g$ defined by

$$\mu_{H_2O} = \mu^0_{H_2O}(T, P) + gkT \log x_{H_2O}, \qquad (903, 2)$$

where

$$g \to 1 \quad (x_{H_2O} \to 1). \qquad (903, 3)$$

If the solute species are ions, the molecular fraction of ions of type $i$ being $x_i$, we can write (2) as

$$\mu_{H_2O} = \mu^0_{H_2O}(T, P) + gkT \log\{1 - \Sigma_i x_i\}, \qquad (903, 4)$$

where

$$g \to 1 \quad (x_i \to 0, \text{ all } i). \qquad (903, 5)$$

All physico-chemical equilibria of the solvent $H_2O$ can be expressed in terms of $\mu_{H_2O}$ and so involve $g$. By straightforward thermodynamics* it can be shown that $g$ is effectively equal to the ratio of the actual freezing-point depression, below that of the pure solvent, to the ideal value for the same value of $\Sigma_i x_i$. It can similarly be shown that $g$ is equal to the ratio of the actual osmotic pressure to the ideal value for the same value of $\Sigma_i x_i$. The quantity $g$ is called the *osmotic coefficient*. It might with as good reason be called the *freezing-point coefficient*.

The osmotic coefficient $g$ is thus an experimental quantity, usually determined by measuring the freezing-point depression and comparing it with the ideal value, *assuming complete dissociation*. Another coefficient, now of

* *M.T.* p. 121.

only historical interest, is the so-called van't Hoff factor $i$, which is the ratio of the actual freezing-point depression to the ideal value, *assuming complete absence of dissociation*. For a single electrolyte, whose molecule gives rise to $2q$ ions, the relation between $i$ and $g$ is

$$i = 2qg, \tag{903, 6}$$

and in particular for a symmetrical (binary) electrolyte

$$i = 2g. \tag{903, 7}$$

The deviation from the ideal form of the partial potentials of each solute ionic species is conveniently measured by the activity coefficient $\gamma_i$ defined by*

$$\mu_i = \mu_i^0(T, P) + kT \log \gamma_i x_i, \tag{903, 8}$$

where

$$\gamma_i \to 1 \quad (x_i \to 0, \text{ all } i). \tag{903, 9}$$

All equilibria involving the ions $i$ are determined by the partial potential† $\mu_i$ and so involve $\gamma_i$.

At constant temperature and pressure the osmotic coefficient $g$ is related thermodynamically to the activity coefficients $\gamma_i$ of the solute ions by the formula‡, due to Bjerrum§,

$$-(1 - \Sigma_i x_i)\, d\{(1-g)\log(1 - \Sigma_i x_i)\} + \Sigma_i x_i\, d \log \gamma_i = 0. \tag{903, 10}$$

Provided the solutions are so dilute that

$$\Sigma_i x_i \ll 1, \tag{903, 11}$$

we may replace (10) by the much simpler and more convenient relation

$$d\{(1-g)\,\Sigma_i c_i\} = \Sigma_i c_i\, d \log \gamma_i. \tag{903, 12}$$

All the solutions with which we shall be concerned in this chapter are sufficiently dilute to justify the replacement of (10) by (12). As pointed out by Bjerrum§, the approximation involved in the use of (12) instead of (10) is much less drastic than the approximation of replacing (4) by

$$\mu_{H_2O} = \mu^0_{H_2O}(T, P) - g\frac{kT}{V} v_{H_2O}\, \Sigma_i N_i. \tag{903, 13}$$

In aqueous solutions of non-electrolytes neither $g$ nor any $\gamma$'s usually deviate appreciably from unity at concentrations below tenth molar

* See *M.T.* p. 115.

† The partial potential $\mu_i$ of an ionic species is not completely determined by the internal composition of the phase, but depends also on the distribution of electric charge at its surface. For this reason the partial potential $\mu_i$ of an ion $i$ is also called its electrochemical potential. Hence $\mu_i^0$ contains a term determined by the (accidental) condition of the surface of the solution. All applications of the $\mu_i$ involve linear combinations such that these terms cancel, the reason being that in order to preserve electric neutrality inside every phase one always considers transfer from one phase to another of electrically neutral combinations of ions. See *M.T.* Chapter x.

‡ See *M.T.* p. 118, formula (559, 2).

§ Bjerrum, *Zeit. Elektrochem.* **24**, 325 (1918); *Zeit. Physikal. Chem.* **104**, 406 (1923).

($c \simeq 0{\cdot}1$), and often not below molar ($c \simeq 1$). In solutions of strong electrolytes, however, $g$ and the $\gamma_i$ deviate appreciably from unity at concentrations as low as thousandth molar ($c \simeq 0{\cdot}001$). These deviations were formerly known as *the anomalies of strong electrolytes*. They are clearly due to the long range electrostatic forces between the charges on the ions, the effects of which form the main subject-matter of this chapter. When account is taken of these effects the anomalies disappear.

**§ 904. General considerations concerning phase integrals. Interionic attraction.** Let us first consider an assembly of $N$ ions, $N_i$ of type $i$, moving freely in a volume $V$ of continuous incompressible medium of dielectric constant $D$, independent of temperature and pressure. We shall later replace this fictitious medium by something more like a real solvent. For this assembly the problem is formally the same as that of imperfect gases, namely the evaluation of the phase integral

$$\Omega = \frac{1}{\Pi_i N_i!}\int\cdots\int e^{-W/kT}\,\Pi_i(d\omega_i)^{N_i}, \tag{904, 1}$$

where $W$ is the potential energy of the assembly of ions for a given configuration, and the integration extends over the $3N$-dimensional configuration space of the $N$ ions. The evaluation of $\Omega$ is, however, rendered incomparably more difficult than for imperfect gases by the long range nature of the electrostatic forces between the ions. $\Omega$ contributes as usual $-kT\log\Omega$ to the free energy.

Since $W$ is by definition the total potential energy of the assembly in a given configuration, $W$ can be written in the form

$$W = W^{\text{short}} + W^{\text{ch}}; \tag{904, 2}$$

$W^{\text{short}}$ is the potential energy due to all the (short range) interactions remaining when the charges are removed; $W^{\text{ch}}$ is the potential energy due to the charges. So defined $W^{\text{ch}}$ would include alterations of $W^{\text{short}}$ by polarization, but this effect will be neglected. Since the assembly is assumed very dilute, $W^{\text{short}}$ is effectively due solely to solvent-solute interactions, and is constant for effectively all configurations of the ions. The assembly would therefore, as we saw in § 823, be ideal were it not for $W^{\text{ch}}$. The free energy of the actual assembly will therefore exceed the free energy with the ions uncharged by the quantity

$$F^{\text{ch}} = -kT\log\int\cdots\int e^{-W^{\text{ch}}/kT}\,\Pi_i(d\omega_i)^{N_i} + NkT\log V. \tag{904, 3}$$

$W^{\text{ch}}$ can be further analysed into

$$W^{\text{ch}} = W^{\text{self}} + W^{\text{el}}; \tag{904, 4}$$

$W^{\text{self}}$ is the self-energy due to charging each ion in the solution in the effective absence of the other ions and is assumed to be independent of the configuration; $W^{\text{el}}$ is the energy due to the mutual electrical interactions of the various ions. We shall assume that

$$W^{\text{el}} = \Sigma_{\alpha\beta} \frac{z_\alpha z_\beta |e|^2}{r_{\alpha\beta} D}, \tag{904, 5}$$

summed over all pairs of ions $\alpha$ and $\beta$, their distance apart being $r_{\alpha\beta}$. We thus ignore the mutual polarization of the ions. We therefore write

$$F^{\text{ch}} = W^{\text{self}} + F^{\text{el}}, \tag{904, 6}$$

$$F^{\text{el}} = -kT \log \int \dots \int e^{-W^{\text{el}}/kT}\, \Pi_i\, (d\omega_i)^{N_i} + NkT \log V. \tag{904, 7}$$

**§ 905. Dimensional considerations. Milner's formula.** Before discussing possible methods of evaluating $\Omega$ and so $F^{\text{el}}$, it is interesting to consider the restrictions on possible forms of $F^{\text{el}}$ imposed by dimensional considerations.* We assume that each ion is characterized by its charge $z|e|$ and its size; we therefore ascribe to each ion an effective diameter $a$. For simplicity we shall at this stage suppose that all the ions have the same numerical valency $|z|$ and the same effective diameter $a$. We assume that the medium is characterized by its volume $V$, its temperature $T$ (or $kT$) and its dielectric constant $D$. The assembly is completely defined by the number $N$ of ions ($\frac{1}{2}N$ of each sign), the nature of the ions and the nature of the medium. It is then clear that $F^{\text{el}}$ must be a function of $N, z|e|, a, V, kT, D$. If we assume that $F^{\text{el}}$ is, apart from pure numbers, a function of these quantities only, then simple dimensional analysis shows that $F^{\text{el}}/NkT$, being a pure number, must be a function of $N^{\frac{1}{3}} z^2 |e|^2 D^{-1} k^{-1} T^{-1} V^{-\frac{1}{3}}$ and of $z^2|e|^2 D^{-1} k^{-1} T^{-1} a^{-1}$, both pure numbers.† No other independent combinations of the independent variables are pure numbers. At extremely high dilutions it is reasonable to expect the sizes of the ions to be irrelevant, the ions being then characterized entirely by their charges. When this is the case $F^{\text{el}}/NkT$ becomes a function of $N^{\frac{1}{3}} z^2 |e|^2 D^{-1} k^{-1} T^{-1} V^{-\frac{1}{3}}$.

The first serious attempt to evaluate $\Omega$ was made by Milner‡ who formulated the problem in an accurate form. He pointed out in a clear manner the difficulties of an exact evaluation of $\Omega$, and attempted to obtain an approximate but direct evaluation. In view of the great mathematical

* Cf. Klein, *Medd. Kong. Vet. Nobelinstitut*, **5**, no. 6 (1919).

† Although $N$ actually denotes the number of ions, we might if we preferred take $N$ to be the number of gr.-ions or Kg.-ions or lb.-ions. Hence for the purpose of dimensional analysis $N$ must here be regarded as a measure of quantity of ions and not as a pure number.

‡ Milner, *Phil. Mag.* **23**, 551 (1912).

difficulties it is remarkable that the approximate result obtained by him can be expressed conveniently in the form

$$\frac{F^{\mathrm{el}}}{NkT} \simeq -A\,\tfrac{2}{3}\pi^{\frac{1}{2}}\left\{\frac{N^{\frac{1}{3}}z^2|e|^2}{V^{\frac{1}{3}}DkT}\right\}^{\frac{3}{2}}, \tag{905, 1}$$

where $A$ is a pure number, for which he obtained two different crude approximations. His results expressed numerically in tabular form correspond to $A \simeq 0{\cdot}70$; an alternative estimate given in a footnote is $A \simeq (\frac{1}{2}\pi)^{\frac{1}{2}} \simeq 1{\cdot}25$. We shall see that an entirely different method of attack due to Debye* leads to a formula of exactly the form (1) with $A = 1$ and so intermediate between Milner's two approximations.

**§ 906. Average potentials and charge densities. Poisson's equation.** As an introduction to Debye's treatment we shall define certain average potentials, and shall consider how they are related to $\Omega$ and to one another. To avoid ambiguity it is desirable to use a specialized notation which we shall now define. Suppose $Q$ to be any property of the assembly depending on its configuration. Then as usual we denote by $\bar{Q}$ the average of $Q$ over all accessible configurations; thus

$$\bar{Q}\int\ldots\int e^{-W/kT}\,(d\omega)^N = \int\ldots\int Qe^{-W/kT}\,(d\omega)^N. \tag{906, 1}$$

We further denote by ${}^{\alpha}\bar{Q}$ the average of $Q$ over all accessible configurations in which the particular ion $\alpha$ is held fixed at a given place; thus

$${}^{\alpha}\bar{Q}\int\ldots\int e^{-W/kT}\,(d\omega)^{N-1} = \int\ldots\int Qe^{-W/kT}\,(d\omega)^{N-1}, \tag{906, 2}$$

where the integrations extend over the coordinates of all the ions except $\alpha$. Finally we denote by ${}^{\alpha\beta}\bar{Q}$ the average of $Q$ over all accessible configurations in which the particular ions $\alpha$ and $\beta$ are each held at given places; thus

$${}^{\alpha\beta}\bar{Q}\int\ldots\int e^{-W/kT}\,(d\omega)^{N-2} = \int\ldots\int Qe^{-W/kT}\,(d\omega)^{N-2}, \tag{906, 3}$$

where the integrations extend over the coordinates of all the ions except $\alpha$ and $\beta$.

In the discussion which follows we shall assume that for any given configuration of ions we can define an electrostatic potential and charge density which obey Poisson's equation. This is itself far from obvious, and really requires us to be allowed to smear out the charges of the ions into continuous

* The original paper is: Debye and Hückel, *Physikal. Zeit.* **24**, 185 (1923), but many features of the original treatment have been corrected and modified subsequently. For references see for example Falkenhagen, *Electrolytes* (Oxford, 1934).

distributions without thereby spreading them over regions within which the electrostatic potential changes appreciably. We cannot attempt to go more deeply into these difficulties here, but it is to be noted that any attempt to apply such smoothing will become more difficult the smaller the collision diameters of the individual ions.

Let $r$ denote the distance from the centre of the ion $\alpha$ (assumed to be spherically symmetrical), $\rho(r)$ the smoothed electrostatic charge density at the distance $r$ from the centre of the ion $\alpha$, and $\psi(r)$ the corresponding electrostatic potential, in any specified configuration of the assembly. The functions $\psi(r)$ and $\rho(r)$ are related by Poisson's equation

$$\nabla^2\psi(r) = -\frac{4\pi}{D}\rho(r). \tag{906, 4}$$

The energy $W$ of the configuration is independent of $r$ which is not a co-ordinate of any ion. If therefore we average over all configurations of the ions other than $\alpha$, we obtain

$$\nabla^2\{{}^{\alpha}\overline{\psi(r)}\} = -\frac{4\pi}{D}{}^{\alpha}\overline{\rho(r)}. \tag{906, 5}$$

We shall see that Debye's treatment is essentially an approximate short cut for evaluating ${}^{\alpha}\overline{\psi(r)}$, and in particular ${}^{\alpha}\overline{\psi(0)}$, the average electrostatic potential at the centre of the ion $\alpha$. This leads simply to the evaluation of $F^{\text{el}}$. For according to (904, 3) and (904, 6), we have

$$W^{\text{self}} + F^{\text{el}} = -kT\log\int\ldots\int e^{-W^{\text{ch}}/kT}\,\Pi_i\,(d\omega_i)^{N_i} + NkT\log V. \tag{906, 6}$$

If we differentiate this with respect to $z_\alpha|e|$, the charge of the ion $\alpha$, we obtain

$$\frac{\partial W^{\text{self}}}{|e|\,\partial z_\alpha} + \frac{\partial F^{\text{el}}}{|e|\,\partial z_\alpha} = \frac{\int\ldots\int\frac{\partial W^{\text{ch}}}{|e|\,\partial z_\alpha}e^{-W^{\text{ch}}/kT}(d\omega)^N}{\int\ldots\int e^{-W^{\text{ch}}/kT}(d\omega)^N} = \overline{\frac{\partial W^{\text{ch}}}{|e|\,\partial z_\alpha}}. \tag{906, 7}$$

Now $\partial W^{\text{ch}}/|e|\,\partial z_\alpha$ is the increase in the energy (averaged over all configurations) of the assembly per unit increase of charge on the ion $\alpha$, and this is equal to the increase in the energy of the assembly per unit increase of charge at the place occupied by the ion $\alpha$, that is to say, the electrostatic potential of the place occupied by the ion $\alpha$. We may therefore replace (7) by

$$\frac{\partial W^{\text{self}}}{|e|\,\partial z_\alpha} + \frac{\partial F^{\text{el}}}{|e|\,\partial z_\alpha} = {}^{\alpha}\overline{\psi(0)}. \tag{906, 8}$$

Now we recall that $\partial W^{\text{self}}/|e|\,\partial z_\alpha$ is merely the part of the electrostatic potential at the centre of $\alpha$ due to its own charge, that is the self potential of the ion $\alpha$; it is of course a property of $\alpha$ independent of the remaining ions.

If we subtract this self potential from ${}^{\alpha}\overline{\psi(0)}$, we obtain the part of the average electrostatic potential at the ion $\alpha$ due to the remaining ions; if we denote this by $\psi_\alpha$, then

$$\psi_\alpha = {}^{\alpha}\overline{\psi(0)} - \frac{\partial W^{\text{self}}}{|e|\,\partial z_\alpha}, \qquad (906,9)$$

and we have

$$\frac{\partial F^{\text{el}}}{|e|\,\partial z_\alpha} = \psi_\alpha. \qquad (906,10)$$

By considering the dependence of $F^{\text{el}}$ on the charge of each one of the ions in the assembly, we obtain

$$dF^{\text{el}} = \psi_\alpha |e|\,dz_\alpha + \psi_\beta |e|\,dz_\beta + \ldots, \qquad (906,11)$$

where each of $\psi_\alpha, \psi_\beta, \ldots$ is a function of all the valencies $z_\alpha, z_\beta, \ldots$. Since $F$ is a single-valued function of the equilibrium state of the assembly, $dF^{\text{el}}$ is a complete differential, and consequently the $\psi_\alpha, \psi_\beta, \ldots$ must be interrelated by

$$\frac{\partial \psi_\alpha}{\partial z_\beta} = \frac{\partial \psi_\beta}{\partial z_\alpha}, \ldots. \qquad (906,12)$$

This relation may be used to check the self-consistency of any approximate formulae for $\psi_\alpha, \psi_\beta, \ldots$.

**§ 907. Probable form of $\psi_\alpha$ and $F^{\text{el}}$.** Before proceeding to Debye's approximate evaluation of $\psi_\alpha$ we shall consider what form we might expect by intelligent guessing. Let us first consider ${}^{\alpha}\overline{\psi(r)}$, the average electrostatic potential at a distance $r$ from the centre of $\alpha$. Its value will depend on the valency $z_\alpha$ of $\alpha$ and also on the valencies $z_\beta, z_\gamma, \ldots$ of all the remaining ions. For simplicity let us suppose that all the remaining ions have the same numerical valency $z$. Then we may reasonably expect that ${}^{\alpha}\overline{\psi(r)}$ can be expanded in a double power series in $z_\alpha$ and $z$. But when $z_\alpha$ is zero the average potential at a distance $r$ from $\alpha$ will not differ from the average potential anywhere in the solution, which is by definition zero. Thus there will be no terms in the double series independent of $z_\alpha$. When, on the other hand, $z$ is zero, ${}^{\alpha}\overline{\psi(r)}$ becomes simply $z_\alpha |e|/Dr$, the potential due to the ion $\alpha$. If then we denote by $\psi_\alpha(r)$ the potential at a distance $r$ from $\alpha$ due to the ions other than $\alpha$, its average value ${}^{\alpha}\overline{\psi_\alpha(r)}$ expressed as a power series in $z_\alpha$ and $z$ will have its lowest term of the order $z_\alpha z$. We may hope that this series will converge so rapidly that we may obtain a useful approximation by retaining only its first term. To this approximation we should have

$${}^{\alpha}\overline{\psi_\alpha(r)} \propto z_\alpha z, \qquad (907,1)$$

and in particular for $r = 0$

$$\psi_\alpha \propto z_\alpha z, \qquad (907,2)$$

and assuming $\alpha$ to have the same numerical valency as all the other ions

$$\psi_\alpha \propto z^2. \tag{907, 3}$$

Comparing (3) with (906, 11) for the special case

$$|z_\alpha| = |z_\beta| = \ldots = z, \tag{907, 4}$$

we deduce

$$F^{\text{el}} \propto z^3. \tag{907, 5}$$

Finally combining (5) with the dimensional conclusions reached in § 905, namely that $F^{\text{el}}/NkT$ is at sufficiently high dilutions a function of $N^{\frac{1}{2}}z^2|e|^2 V^{-\frac{1}{2}}D^{-1}k^{-1}T^{-1}$, we deduce that

$$\frac{F^{\text{el}}}{NkT} = -A'\left\{\frac{N^{\frac{1}{2}}z^2|e|^2}{V^{\frac{1}{2}}DkT}\right\}^{\frac{3}{2}}. \tag{907, 6}$$

We saw in § 905 that this is precisely the form of approximation obtained by Milner. We shall also find that Debye's treatment leads to a formula agreeing with (6) with $A' = 2\pi^{\frac{1}{2}}/3$. It will thus appear that Debye's approximation corresponds closely to what we have here described as intelligent guessing.

§ 908. **Boltzmann's formula.** By the arguments used in § 702, the frequency of occurrence of an ion $\beta$ in an element of volume $d\omega$ anywhere in the assembly is $d\omega/V$, but if the element of volume is specified to be at a distance $r$ from a given ion $\alpha$ the frequency of occurrence of the ion $\beta$ in it will be of the form

$$e^{-W_{\alpha\beta}/kT}\, d\omega/V. \tag{908, 1}$$

This formula is of the familiar form of Boltzmann's formula. It is, however, important to be clear about the meaning of $W_{\alpha\beta}$, which has been fully discussed in § 702 in connection with imperfect gases. The quantity $W_{\alpha\beta}$ may be described alternatively as

(*a*) The average "free energy" of an ion $\beta$ at a distance $r$ from a given ion $\alpha$.

(*b*) The work required to bring an ion $\beta$ from infinity to a distance $r$ from an ion $\alpha$ averaged over all configurations of the remaining ions.

(*c*) The potential energy whose derivative gives the average force acting on the ion $\beta$ in the given element, distant $r$ from the given ion $\alpha$

Any of these definitions is equivalent to the relation

$$\frac{e^{-W_{\alpha\beta}/kT}}{V^2}\int\ldots\int e^{-W/kT}\,(d\omega)^N = \int\ldots\int e^{-W/kT}\,(d\omega)^{N-2}, \tag{908, 2}$$

the first integration extending over all configurations of all the ions, the second extending over all configurations of all ions other than $\alpha$ and $\beta$, these being held fixed. Let us differentiate (2) with respect to $x_\beta$, one of the

coordinates of the position occupied by the ion $\beta$. The integral on the left extends over all configurations of all ions and is therefore independent of $x_\beta$, but the integral on the right extends only over configurations with $x_\alpha$, $x_\beta$ specified and therefore depends on $x_\alpha$, $x_\beta$. If we take logarithms and then differentiate, we obtain

$$\frac{\partial W_{\alpha\beta}}{\partial x_\beta} = \frac{\int \dots \int \frac{\partial W}{\partial x_\beta} e^{-W/kT} (d\omega)^{N-2}}{\int \dots \int e^{-W/kT} (d\omega)^{N-2}}, \tag{908, 3}$$

or in the notation defined in § 906

$$\frac{\partial W_{\alpha\beta}}{\partial x_\beta} = {}^{\alpha\beta}\overline{\frac{\partial W}{\partial x_\beta}}, \tag{908, 4}$$

thus confirming the definition (*c*) of $W_{\alpha\beta}$.

From the definition (*b*) of $W_{\alpha\beta}$ it is evident that we must have

$$W_{\alpha\beta} = W_{\beta\alpha}. \tag{908, 5}$$

This relation may be used as a check on the consistency of any approximate formula for $W_{\alpha\beta}$.

**§ 909. Relation between $^{\alpha}\overline{\psi(r)}$ and $W_{\alpha\beta}$.** From formula (908, 1) for the frequency of occurrence of a given ion $\beta$ in an element of volume $d\omega$ at a distance $r$ from the ion $\alpha$, we obtain for the average charge density $^{\alpha}\overline{\rho(r)}$ at a distance $r$ from the ion $\alpha$

$$^{\alpha}\overline{\rho(r)} = \Sigma_\beta z_\beta |e| \, e^{-W_{\alpha\beta}/kT}/V. \tag{909, 1}$$

If we substitute from (1) into Poisson's equation (906, 5), we obtain the equation

$$\nabla^2\{^{\alpha}\overline{\psi(r)}\} = -\frac{4\pi}{DV} \Sigma_\beta z_\beta |e| \, e^{-W_{\alpha\beta}/kT}. \tag{909, 2}$$

This formula is exact, apart from errors due to smoothing, provided that $^{\alpha}\overline{\psi(r)}$ and $W_{\alpha\beta}$ are defined as above.

**§ 910. Debye's approximation.** The fundamental approximation of Debye* may be expressed as

$$W_{\alpha\beta} = z_\beta |e| \, ^{\alpha}\overline{\psi(r)}. \tag{910, 1}$$

Since by definition

$$W_{\alpha\beta} = W_{\beta\alpha}, \tag{910, 2}$$

the assumption (1) implies

$$z_\beta \, ^{\alpha}\overline{\psi(r)} = z_\alpha \, ^{\beta}\overline{\psi(r)}. \tag{910, 3}$$

* Debye and Huckel, *Physikal. Zeit.* **24**, 185 (1923). The nature of the approximation is by no means made clear in the original papers.

This can be true for all possible pairs of ions only if

$$\frac{{}^{\alpha}\overline{\psi(r)}}{z_{\alpha}} = \frac{{}^{\beta}\overline{\psi(r)}}{z_{\beta}} = \dots \tag{910, 4}$$

The relations (4) can serve to check the self-consistency of any approximate solution of the problem.

If we substitute (1) into (909, 2), we obtain Debye's equation

$$\nabla^2\{{}^{\alpha}\overline{\psi(r)}\} = -\frac{4\pi}{DV}\Sigma_{\beta} z_{\beta}|e|\, e^{-z_{\beta}|e|\,{}^{\alpha}\overline{\psi(r)}/kT}. \tag{910, 5}$$

We now abbreviate ${}^{\alpha}\overline{\psi(r)}$ to $\psi(r)$ and rewrite (5) as*

$$\nabla^2\psi(r) = -\frac{4\pi}{DV}\Sigma_i N_i z_i|e|\, e^{-z_i|e|\psi(r)/kT}. \tag{910, 6}$$

It is customary to refer to (6) as the Poisson-Boltzmann equation. It is an approximation dependent on the assumption (1).

**§ 911. Debye's solution.** The Poisson-Boltzmann equation (910, 6) requires to be solved with the appropriate boundary conditions. These are first that $\psi(r)$ and $\partial\psi/\partial r$ vanish at infinity, and second that the electric induction be continuous at the boundary between the ion $\alpha$ and the surrounding solution.

In principle (910, 6) is soluble as it stands, but requires elaborate treatment. The further approximation made by Debye to render it soluble in finite terms is to assume that $|e||z_i\psi(r)|/kT$ is small compared with unity for all important values of $r$. We then expand the exponential as a power series and note that, owing to the condition of electrical neutrality

$$\Sigma_i N_i z_i = 0, \tag{911, 1}$$

the first term vanishes. Debye neglects all terms higher than the second and so obtains the approximation

$$\nabla^2\psi(r) = \kappa^2\psi(r), \tag{911, 2}$$

where $\kappa$ is defined by

$$\kappa^2 = \frac{4\pi\Sigma_i N_i z_i^2|e|^2}{VDkT}, \quad \kappa > 0. \tag{911, 3}$$

The most general spherically symmetrical solution of (3), which is finite at $r = \infty$, is

$$\psi(r) = \frac{A}{r}e^{-\kappa r}, \tag{911, 4}$$

with $A$ constant.

* We use the subscripts $\alpha$, $\beta$ to refer to individual ions and the subscript $i$ to denote types of ions. This summation over $\beta$ is equivalent to multiplication by $N_i$ followed by summation over all $i$'s.

To obtain the value of $A$, we take the ions to be rigid spheres with closest distance of approach (diameter) equal to $a$. The solution (4) then applies to all values of $r \geqslant a$. The electric induction in the radial direction according to (4) is

$$-D\frac{\partial \psi}{\partial r} = \frac{DA}{r^2} e^{-\kappa r}(1+\kappa r) \quad (r \geqslant a). \tag{911, 5}$$

But for $r$ just less than $a$, since there can be no other ion present, the electric induction is due entirely to the charge on the ion $\alpha$ and is therefore

$$\frac{z_\alpha |e|}{a^2}. \tag{911, 6}$$

For continuity of the electric induction at $r = a$ the expressions (5) and (6) must be equal. Thus

$$D\frac{A}{a^2} e^{-\kappa a}(1+\kappa a) = \frac{z_\alpha |e|}{a^2}. \tag{911, 7}$$

Solving (7) for $A$ and substituting into (4), we obtain

$$\psi(r) = \frac{z_\alpha |e|}{Dr} \frac{e^{-\kappa(r-a)}}{1+\kappa a}, \tag{911, 8}$$

and in particular the value at $r = a$ is

$$\psi(a) = \frac{z_\alpha |e|}{Da} \frac{1}{1+\kappa a}. \tag{911, 9}$$

If we now subtract from $\psi(a)$ the self potential of the ion $\alpha$ at $r = a$, we obtain for $\psi_\alpha$, the electrostatic potential for $r \leqslant a$ due to the remaining ions,

$$\psi_\alpha = \frac{z_\alpha |e|}{Da} \frac{1}{1+\kappa a} - \frac{z_\alpha |e|}{Da} = -\frac{z_\alpha |e|}{D} \frac{\kappa}{1+\kappa a}. \tag{911, 10}$$

§ **912. Self-consistency of solution.** Without at this stage analysing the legitimacy of Debye's approximations, we can verify that his solution is self-consistent. Firstly we see from (911, 8) that $\overset{\alpha}{\overline{\psi(r)}}$ is directly proportional to $z_\alpha$ and so the conditions (910, 4) are satisfied. Secondly we must verify the conditions (906, 12)

$$\frac{\partial \psi_\alpha}{\partial z_\beta} = \frac{\partial \psi_\beta}{\partial z_\alpha}. \tag{912, 1}$$

The formula for $\kappa^2$ can be written

$$\kappa^2 = \frac{4\pi(z_\alpha^2 + z_\beta^2 + \ldots)|e|^2}{VDkT}, \tag{912, 2}$$

where the unspecified summation extends over all ions, and so

$$\frac{\partial \kappa}{\partial z_\beta} = \frac{4\pi z_\beta |e|^2}{\kappa VDkT}. \tag{912, 3}$$

By differentiating (911, 10) with respect to $z_\beta$ and using (3), it can be verified that $\partial\psi_\alpha/\partial z_\beta$ contains the factor $z_\alpha z_\beta$ and otherwise depends on $z_\alpha$ and $z_\beta$ only through $\kappa$. It follows that $\partial\psi_\alpha/\partial z_\beta$ is symmetrical in $\alpha$, $\beta$ and so (1) is verified.

We emphasize the self-consistency of Debye's solution because, when attempts are made to solve the Poisson-Boltzmann equation (910, 6) more accurately, they lead to solutions lacking this self-consistency and it is therefore by no means certain that such solutions are any more valuable than that given by Debye.

It is of interest to verify that Debye's solutions satisfy the condition of electrical neutrality. The total charge surrounding the ion $\alpha$ is given by

$$\int_a^\infty \overline{{}^\alpha\rho(r)}\, 4\pi r^2 dr, \qquad (912, 4)$$

or, by using Poisson's equation,

$$-\frac{D}{4\pi}\int_a^\infty \nabla^2\{\overline{{}^\alpha\psi(r)}\}\, 4\pi r^2 dr. \qquad (912, 5)$$

According to Debye's approximation (911, 2) this becomes

$$-\frac{D}{4\pi}\int_a^\infty \kappa^2\, \overline{{}^\alpha\psi(r)}\, 4\pi r^2 dr. \qquad (912, 6)$$

Substituting from (911, 8) this becomes

$$-\frac{D}{4\pi}\int_a^\infty \kappa^2 \frac{z_\alpha|e|\, e^{-\kappa(r-a)}}{Dr(1+\kappa a)}\, 4\pi r^2 dr$$
$$= -z_\alpha|e|\frac{e^{\kappa a}}{1+\kappa a}\int_{\kappa a}^\infty e^{-\kappa r}\kappa r\, d(\kappa r) = -z_\alpha|e|, \qquad (912, 7)$$

so that the total charge surrounding any given ion $\alpha$ is just equal and opposite to the charge on $\alpha$, as it should be.

**§ 913. Free energy.** Having verified the integrability condition (906, 12), we can substitute the value of $\psi_\alpha$ from (911, 10) into (906, 11) and integrate to obtain $F^{\text{el}}$. The order of integration being immaterial, it is most convenient during the integration to increase the charges of all the ions in the same ratio. If we denote by $\lambda$ the fraction of their final charges which the ions have at any stage of the integration, then we have

$$F^{\text{el}} = \int_0^1 \Sigma_\alpha\, \psi_\alpha(\lambda)\, z_\alpha|e|\, d\lambda = \int_0^1 \Sigma_i\, N_i\, \psi_i(\lambda)\, z_i|e|\, d\lambda$$
$$= -\int_0^1 \Sigma_i\, N_i \frac{\lambda z_i|e|}{D}\frac{\lambda\kappa}{1+\lambda\kappa a} z_i|e|\, d\lambda = -\Sigma_i \frac{N_i z_i^2|e|^2\kappa}{D}\int_0^1 \frac{\lambda^2 d\lambda}{1+\lambda\kappa a}$$
$$= -\frac{\Sigma_i N_i z_i^2|e|^2\kappa}{3D}\tau(\kappa a), \qquad (913, 1)$$

where $\tau(x)$ is the function

$$\tau(x) = \frac{3}{x^3}[\log(1+x) - x + \tfrac{1}{2}x^2]$$

$$= 1 - \tfrac{3}{4}x + \tfrac{3}{5}x^2 - \tfrac{3}{6}x^3 + \tfrac{3}{7}x^4 - \dots. \qquad (913, 2)$$

For small $\kappa a$, that is for high dilutions, $\tau(\kappa a) \to 1$. We then have

$$F^{\text{el}} = -\frac{\Sigma_i N_i z_i^2 |e|^2 \kappa}{3D}$$

$$= -\frac{1}{3}\left\{\frac{\Sigma_i N_i z_i^2 |e|^2}{D}\right\}^{\frac{3}{2}} \left(\frac{4\pi}{VkT}\right)^{\frac{1}{2}}. \qquad (913, 3)$$

If all the ions have the same numerical valency $z$ and there are $\frac{1}{2}N$ of each sign, (3) reduces to

$$\frac{F^{\text{el}}}{NkT} = -\tfrac{2}{3}\pi^{\frac{1}{2}} \left\{\frac{N^{\frac{1}{3}} z^2 |e|^2}{V^{\frac{1}{3}} DkT}\right\}^{\frac{3}{2}}, \qquad (913, 4)$$

as already quoted in § 905.

**§ 914. Mean thickness of ionic atmosphere.** If we divide the space surrounding a given ion $\alpha$ into spherical shells of the same thickness $dr$, then according to (912, 7) the net charge in each such shell is equal to

$$-z_\alpha |e| \frac{e^{\kappa a}}{1+\kappa a} \kappa^2 e^{-\kappa r} r\, dr. \qquad (914, 1)$$

This has a maximum value for $r$ given by

$$\frac{d}{dr}\{e^{-\kappa r} r\} = 0, \qquad (914, 2)$$

or

$$r = 1/\kappa. \qquad (914, 3)$$

For this reason $1/\kappa$ is often called the mean thickness of the ionic atmosphere.

Since according to (911, 3) $1/\kappa$ is proportional to the square root of $V$, it follows that the mean thickness of the ionic atmosphere increases as the square root of the dilution. If we insert numerical values into (911, 3) and introduce the ionic strength $I$ defined by

$$I = \frac{10^3 \Sigma_i N_i z_i^2}{2\mathbf{N} V}, \qquad (914, 4)$$

so that for a uni-univalent electrolyte the ionic strength is equal to the concentration in moles/litre, we obtain in water at 0° C., using $D = 88{\cdot}23$,

$$\kappa = 0{\cdot}324 \times 10^8 I^{\frac{1}{2}} \text{ cm.}^{-1}, \qquad (914, 5)$$

$$\frac{1}{\kappa} = \frac{3{\cdot}08}{I^{\frac{1}{2}}} \text{Å}. \qquad (914, 6)$$

Thus for an ionic strength of 0·01 the mean thickness of the atmosphere is

about 30 Å. For an ionic strength 1 the value of $1/\kappa$ is only 3 Å. and is comparable to the diameter of an ion. At such concentrations it is extremely unlikely that the various approximations remain valid. In view of the smoothing requirements already mentioned the theory is hardly likely to be valid unless $1/\kappa \ll a$, so that the important region of the oppositely charged atmosphere around each ion is well away from its own surface. It is also necessary for the approximations to be valid that Debye's assumption and approximation given in § 910 and § 911 should hold good. These will be discussed later in § 921.

**§ 915. Dependence on dielectric constant.** The assembly so far considered consists of spherical ions moving freely in a volume $V$ of a continuous incompressible medium of dielectric constant $D$ independent of temperature, pressure, and the presence of the ions. Actually the solvent is not a continuous medium, nor is its dielectric constant independent of temperature, pressure, and the presence of the ions. We must therefore consider the effect of these discrepancies between the real solution and the model.

The introduction of a dielectric constant involves averaging over the solvent molecules. This preliminary averaging is unavoidable, and the important question is whether the best effective value for the dielectric constant is its macroscopic value. For calculating the force between two ions separated by several solvent molecules the use of the macroscopic dielectric constant is probably a reasonable approximation, but for a pair of molecules in contact its introduction is almost absurd. We have seen that the mean thickness of the oppositely charged atmosphere around each ion is $1/\kappa$. We may then take $1/\kappa$ as a crude measure of the order of magnitude of the distance apart of pairs of ions making important contributions to $F^{el}$. We may therefore expect the use of the macroscopic dielectric constant to be reasonable when $1/\kappa \gg a$. In aqueous solutions at room temperature, this condition is well satisfied at an ionic strength 0·01 when $1/\kappa \simeq 10a$, but not at all at an ionic strength 1 when $1/\kappa \simeq a$.

If we suppose the conditions justify the use of the macroscopic dielectric constant, the next question is whether the value to be used is that of the pure solvent or some other value determined by the composition of the solution. It was pointed out by Hückel* that, owing to electrical saturation around each ion, the effective dielectric constant in an ionic solution will be less than that of the pure solvent. If $D$ is the effective dielectric constant of the solution, and $D_0$ that of the pure solvent, then the self energy of each

* Hückel, *Physikal. Zeit.* **26**, 93 (1925).

ion $\alpha$ in the solution will exceed that at infinite dilution by an expression of the form

$$\frac{z_\alpha^2|e|^2}{2b_\alpha}\left(\frac{1}{D}-\frac{1}{D_0}\right), \tag{915, 1}$$

where $b_\alpha$ is an effective ionic radius. This will contribute to $F^{el}$ an extra term

$$\Sigma_i \frac{N_i z_i^2|e|^2}{2b_i}\left(\frac{1}{D}-\frac{1}{D_0}\right). \tag{915, 2}$$

Hückel assumed empirically that $D$ varies linearly with the composition of the solution, and deduced that the expression (2) will be roughly proportional to the square of the ionic concentration. But the expression (2) will not be the only correction to $F^{el}$ due to variation of dielectric constant. We obtained formula (913, 1) for $F^{el}$ by integrating an expression from $z_\alpha, z_\beta, \ldots$ all zero to their actual values. If we admit that $D$ depends on the ionic concentration, its value will also vary during this integration. The value of $D$ to be used in (913, 1) is then not that of the solution nor that of the pure solvent but an intermediate value. We therefore conclude that Hückel's correction to (913, 1) is not only empirical but incomplete.* We may, with as good justification and greater simplicity, use for $D$ the value of the dielectric constant of the pure solvent, realizing that with increasing concentration this will become increasingly inaccurate. We may expect that such deviations, as well as other deviations, between (913, 1) and the actual value of $F^{el}$ may be expressed empirically by a power series in the concentrations, the lowest term being proportional to the first power of the concentration.

The restriction on the dielectric constant which it is most necessary to remove is the assumption that it is independent of the temperature. The dielectric constant of the medium has been introduced as a parameter entirely external to the distribution laws of the assembly. In fact $D$ is temperature (and pressure) dependent, showing thereby that it is strictly a property derived from the distribution laws—namely from the orientations of the molecular dipoles of the solvent. In forming other thermodynamic functions from $F^{el}$ this variation of $D$ with $T$ must be taken into account. Though to do this is essential to preserve the ordinary thermodynamic relationships, and must be a better approximation to the truth than ignoring the variation of $D$ altogether, we have no right to assume that the terms so derived are exactly correct. $D$ has entered our equations as a coefficient in certain energy terms and strictly speaking all energy terms (before averaging begins) must be functions only of configurations. In calculating the free

* For other objections to Hückel's formulae see Güntelberg, *Zeit. Physikal. Chem.* **123**, 245 (1926).

energy it is necessary to form this complete configurational energy $W$ and evaluate $\int \ldots \int e^{-W/kT}\,(d\omega)^N$ integrated over all possible configurations in a single stage. In allowing a temperature variable $D$ to enter our $W$ we have already approximated illegitimately by averaging in two stages, first over the dipole orientations and then over the ionic configurations. A series of successive partial averagings cannot give exactly the true result. Nevertheless this successive partial averaging is all that we can attempt to carry through, and the results given by it should be of the correct form and order of magnitude. To this degree of approximation the temperature variation of $D$ is irrelevant to the evaluation of $\Omega$. Since $F^{el}$ is directly related to $\Omega$ its evaluation is also unaffected by the temperature variation of $D$, except in so far as at each temperature the appropriate value of $D$ must be used. In deducing $E^{el}$, the extra internal energy due to the interionic forces, the temperature variation of $D$ is, however, important.

The relation between $E^{el}$ and $F^{el}$ then becomes

$$E^{el} = -T^2\left(\frac{\partial}{\partial T} + \frac{\partial D}{\partial T}\frac{\partial}{\partial D}\right)\frac{F^{el}}{T}. \tag{915, 3}$$

The original formula of Debye contained only the term in $\partial/\partial T$. The thermodynamic discrepancy between Debye's formula for $F^{el}$ and $E^{el}$ was pointed out by Güntelberg and the discrepancy was removed by Bjerrum* by the insertion of the term in $\partial/\partial D$. Bjerrum at the same time explained how the energy corresponding to this extra term resides in the orientation of the solvent molecules.

If we take into account the thermal expansion of the solution, the value of $V$, the volume of the whole assembly, will depend on the temperature. The formula for $E^{el}$ must then be further modified† to

$$E^{el} = -T^2\left(\frac{\partial}{\partial T} + \frac{\partial D}{\partial T}\frac{\partial}{\partial D} + \frac{\partial V}{\partial T}\frac{\partial}{\partial V}\right)\frac{F^{el}}{T}. \tag{915, 4}$$

The remaining restrictions that the solvent be incompressible and have a dielectric constant independent of pressure are less important. They are more conveniently removed at a later stage. As long as they are retained, we have the equalities

$$G^{el} = F^{el}, \quad H^{el} = E^{el}, \quad V^{el} = 0, \tag{915, 5}$$

where the superscript $^{el}$ in each case refers to the excess of the value of the function for the actual solution over its value for an ideal solution of the same temperature, pressure and composition.

* Bjerrum, *Zeit. Physikal. Chem.* **119**, 145 (1926).

† Scatchard, *J. Am. Chem. Soc.* **53**, 2037 (1931); Gatty, *Phil. Mag.* **11**, 1082 (1931).

**§ 916. The ionic diameter.** The quantity $a$ called the mean ionic diameter, or mean distance of closest approach of two ions, occurs in the formula (913, 1) only through the factor $\tau(\kappa a)$, and we know that

$$\tau(\kappa a) \to 1 \quad (\kappa a \to 0). \tag{916, 1}$$

Hence for sufficiently small $\kappa a$ the equilibrium properties become independent of $a$. Since $\kappa$ is proportional to the square root of the ionic strength, we see that at sufficiently high dilutions the equilibrium properties are independent of $a$. We then obtain the so-called limiting formula of Debye

$$F^{\mathrm{el}} = -\frac{\Sigma_i N_i z_i^2 |e|^2}{3D}\kappa, \tag{916, 2}$$

independent of $a$. Algebraically (1) can be satisfied by making $a$ zero, when we should again obtain (2). Formula (2) on this account is often referred to erroneously as valid for point charges. Actually an assembly of point charges is easily proved unstable* and could not exist. In fact the smaller the ions the less justifiable is the approximation leading to (911, 2) and so the less valid are Debye's formulae. The very existence of the assembly of ions depends on their having a finite closest distance of approach, and any valid treatment must recognize this.

As we have just seen the parameter $a$ occurs only through the product $\kappa a$, which is equal to the ratio of the ionic diameter $a$ to the mean thickness of the ionic atmosphere $1/\kappa$. It is therefore clear that as the dilution is increased and the oppositely charged atmosphere becomes more diffuse, the immediate neighbourhood of the ion becomes less important and so the average properties become independent of $a$. On the other hand, as the concentration increases the interaction between pairs of ions near together becomes increasingly important. It is then more than doubtful whether the short-range forces between ions, which are superposed on the Coulomb forces, can be adequately represented by treating the ions as rigid spheres. No attempt has yet been made to compute the effect of dispersion energy and overlap energy superposed on the Coulomb energy in an assembly of free ions. We therefore have no better approximation available than the use of a diameter $a$ of the ions treated as rigid spheres. It should, however, be remembered that thus used the parameter $a$ is quasi-empirical, and must not be expected to be independent of temperature.† We have accordingly to replace (915, 4) by

$$E^{\mathrm{el}} = -T^2\left(\frac{\partial}{\partial T} + \frac{\partial D}{\partial T}\frac{\partial}{\partial D} + \frac{\partial V}{\partial T}\frac{\partial}{\partial V} + \frac{\partial a}{\partial T}\frac{\partial}{\partial a}\right)\frac{F^{\mathrm{el}}}{T}. \tag{916, 3}$$

* Kramers, *Proc. Sect. Sci. Amsterdam*, **30**, 145 (1927).

† Gross and Halpern, *Physikal. Zeit.* **26**, 403 (1925); Bjerrum, *Trans. Fara. Soc.* **23**, 445 (1927).

**§ 917. Effect of compressibility.** We have up to the present assumed that the volume $V$ is invariable, that is unaffected by pressure and by the charges of the ions. In particular formulae (906, 10) and (906, 11) state that in the imaginary process of gradually increasing the charges of the ions the increase of the free energy $F$ is equal to the electrical work done on the assembly. This implies that there is no other work done on the assembly and in particular no work by the external pressure. This implies indirectly that there is no change of volume during the charging process and therefore, if the solution is compressible, this requires an alteration of pressure to maintain the volume constant. The only useful meaning of $F^{el}$ (and a similar remark applies to all related quantities) is the excess of $F$ for the actual solution over its value for an ideal solution at the same temperature and *at the same pressure*. To evaluate $F^{el}$ and related quantities we must therefore make the integration correspond to the charging of the ions at constant pressure. Superposed on the purely electrical work given by the right side of (906, 11) there will be the work done on the system by the external pressure $P$. Instead of (906, 11) we have therefore

$$dF^{el} = \psi_\alpha |e|\, dz_\alpha + \psi_\beta |e|\, dz_\beta + \ldots - P dV, \qquad (917, 1)$$

or since we are assuming $P$ kept constant during the charging process

$$dG^{el} = dF^{el} + d(PV^{el}) = \psi_\alpha |e|\, dz_\alpha + \psi_\beta |e|\, dz_\beta + \ldots. \qquad (917, 2)$$

When we insert the values of $\psi_\alpha, \psi_\beta, \ldots$ given by (911, 9) and integrate, we obtain instead of (913, 1) the more accurate

$$G^{el} = -\frac{\Sigma_i N_i z_i^2 |e|^2 \kappa}{3D} \tau(\kappa a). \qquad (917, 3)$$

In performing the integration of (2) we have ignored the variation of $\kappa$ due to the change of $V$. Hence strictly the value of $\kappa$ to be inserted into (3) is

$$\kappa = \left\{ \frac{4\pi \Sigma_i N_i z_i^2 |e|^2}{DkT\bar{V}} \right\}^{\frac{1}{2}}, \qquad (917, 4)$$

where $\bar{V}$ is an average volume intermediate between the volume $V$ of the actual solution and the volume $V^0$ of the ideal solution of discharged ions. It is easily verified that

$$V^{el} \ll V, \qquad (917, 5)$$

and consequently that, in evaluating the integral for $G^{el}$ the inaccuracy of ignoring the distinction between $V^0$ and $V$ is entirely negligible.

From the corrected formula (3) for $G^{el}$ we can derive all the remaining equilibrium properties by means of general thermodynamic relations. In particular

$$V^{el} = \partial G^{el} / \partial P, \qquad (917, 6)$$

$$F^{el} = G^{el} - P\,\partial G^{el}/\partial P, \tag{917,7}$$

$$H^{el} = G^{el} - T\,\partial G^{el}/\partial T, \tag{917,8}$$

$$E^{el} = G^{el} - T\,\partial G^{el}/\partial T - P\,\partial G^{el}/\partial P, \tag{917,9}$$

$$\mu_i^{el} = \partial G^{el}/\partial N_i. \tag{917,10}$$

**§ 918. Osmotic coefficient and activity coefficients.** From the formula for $G^{el}$

$$G^{el} = -\frac{\Sigma_i N_i z_i^2 |e|^2 \kappa}{3D}\tau(\kappa a), \tag{918,1}$$

where $\tau(x)$ is the function

$$\tau(x) = \frac{3}{x^3}\{\log(1+x) - x + \tfrac{1}{2}x^2\}$$

$$= 1 - \tfrac{3}{4}x + \tfrac{3}{5}x^2 - \tfrac{3}{6}x^3 + \tfrac{3}{7}x^4 - \ldots, \tag{918,2}$$

we deduce for $\mu_{H_2O}^{el}$ the contribution of the interionic forces to the partial potential of the solvent, assumed to be water,

$$\mu_{H_2O}^{el} = \frac{\partial G^{el}}{\partial N_{H_2O}} = \frac{\partial G^{el}}{\partial \kappa}\frac{\partial \kappa}{\partial V}\frac{\partial V}{\partial N_{H_2O}}$$

$$= \frac{\Sigma_i N_i z_i^2 |e|^2}{3D}\frac{\kappa}{2V}V_{H_2O}\sigma(\kappa a), \tag{918,3}$$

where $V_{H_2O}$ denotes the molecular volume of the solvent, and $\sigma(x)$ is the function

$$\sigma(x) = \frac{3}{x^3}\left\{1 + x - \frac{1}{1+x} - 2\log(1+x)\right\}$$

$$= 1 - 3.\tfrac{2}{4}x + 3.\tfrac{3}{5}x^2 - 3.\tfrac{4}{6}x^3 + 3.\tfrac{5}{7}x^4 - \ldots. \tag{918,4}$$

Values of $\sigma(x)$, as also of $\tau(x)$, are given[A] in Table 1 for round values of $x^2$. For high dilutions where $\kappa a \ll 1$ the function $\sigma(\kappa a) \to 1$.

TABLE 1

*Values of the functions $\tau(x)$ and $\sigma(x)$ for round values of $x^2$*

| $x^2$ | $x$ | $\tau(x)$ | $\sigma(x)$ | $x^2$ | $x$ | $\tau(x)$ | $\sigma(x)$ |
|---|---|---|---|---|---|---|---|
| 0·000 | 0·0000 | 1·000 | 1·000 | 0·030 | 0·1732 | 0·886 | 0·786 |
| 0·001 | 0·0316 | 0·976 | 0·954 | 0·040 | 0·2000 | 0·870 | 0·759 |
| 0·002 | 0·0447 | 0·967 | 0·936 | 0·050 | 0·2236 | 0·857 | 0·738 |
| 0·003 | 0·0557 | 0·960 | 0·922 | 0·060 | 0·2449 | 0·846 | 0·717 |
| 0·004 | 0·0633 | 0·954 | 0·912 | 0·070 | 0·2646 | 0·835 | 0·700 |
| 0·005 | 0·0707 | 0·949 | 0·902 | 0·080 | 0·2828 | 0·827 | 0·685 |
| 0·006 | 0·0775 | 0·945 | 0·893 | 0·090 | 0·3000 | 0·819 | 0·671 |
| 0·007 | 0·0837 | 0·941 | 0·886 | 0·100 | 0·3162 | 0·811 | 0·659 |
| 0·008 | 0·0894 | 0·937 | 0·879 | 0·110 | 0·3317 | 0·803 | 0·646 |
| 0·009 | 0·0947 | 0·934 | 0·871 | 0·120 | 0·3464 | 0·796 | 0·636 |
| 0·010 | 0·1000 | 0·931 | 0·866 | 0·150 | 0·3873 | 0·778 | 0·607 |
| 0·020 | 0·1414 | 0·905 | 0·818 | 0·200 | 0·4472 | 0·752 | 0·569 |

[A] See appendix, § A 9.

For extremely dilute solutions, and it is to such only that Debye's theory is applicable, the osmotic coefficient $g$ may with sufficient accuracy be defined by (903, 13) and its relation to $\mu^{el}_{H_2O}$ is then

$$\mu^{el}_{H_2O} = (1-g)\, v_{H_2O} \frac{kT}{V} \Sigma_i N_i. \tag{918, 5}$$

Comparing (5) with (3) we obtain for $g$

$$1-g = \frac{|e|^2 \kappa}{6DkT} \frac{\Sigma_i N_i z_i^2}{\Sigma_i N_i} \sigma(\kappa a). \tag{918, 6}$$

For $\mu^{el}_i$ the contribution of the interionic forces to the partial potential of an ion we obtain

$$\mu^{el}_i = \frac{\partial G}{\partial N_i} = -\frac{z_i^2|e|^2}{2D} \frac{\kappa}{1+\kappa a} + \frac{\Sigma_i N_i z_i^2 |e|^2}{3D} \frac{\kappa}{2V} V_i \sigma(\kappa a), \tag{918, 7}$$

where $V_i$ denotes the molecular volume of the ion $i$. According to the definition (903, 8) of the activity coefficient $\gamma_i$, this is related to $\mu^{el}_i$ by

$$kT \log \gamma_i = \mu^{el}_i. \tag{918, 8}$$

Substituting from (7) into (8) we obtain

$$\log \gamma_i = -\frac{z_i^2|e|^2}{2DkT} \frac{\kappa}{1+\kappa a} + \frac{\kappa^3 V_i}{24\pi} \sigma(\kappa a). \tag{918, 9}$$

At all concentrations at which Debye's theory is at all applicable $\kappa^3 V_i \ll 1$ and the second term of (9) is entirely negligible compared with the first, so that (9) simplifies to

$$\log \gamma_i = -\frac{z_i^2|e|^2}{2DkT} \frac{\kappa}{1+\kappa a}. \tag{918, 10}$$

The activity coefficients of individual ions are convenient mathematical fictions.* It is only the partial potentials and mean activity coefficients of electrolytes that are physically significant. The mean activity coefficient $\gamma_\pm$ of an electrolyte, whose molecule yields $q_+$ cations of valency $z_+$ and $q_-$ anions of valency $z_-$, is related to the ionic activity coefficients $\gamma_+$, $\gamma_-$ by

$$\log \gamma_\pm = \frac{q_+ \log \gamma_+ + q_- \log \gamma_-}{q_+ + q_-}. \tag{918, 11}$$

Substituting from (10) we obtain

$$\log \gamma_\pm = -\frac{q_+ z_+^2 + q_- z_-^2}{q_+ + q_-} \frac{|e|^2}{2DkT} \frac{\kappa}{1+\kappa a}. \tag{918, 12}$$

By using the condition of electrical neutrality

$$q_+ z_+ + q_- z_- = 0, \tag{918, 13}$$

* Taylor, *J. Phys. Chem.* **31**, 1478 (1927); Guggenheim, *J. Phys Chem.* **33**, 842 (1929). See also footnote †, p. 382.

this can be transformed to

$$\log \gamma_{\pm} = -\frac{z_+|z_-|\,|e|^2}{2DkT}\frac{\kappa}{1+\kappa a}. \qquad (918, 14)$$

**§ 919. Comparison with experiment.** If we insert numerical values into (918, 6) and introduce the ionic strength $I$ defined by

$$I = \frac{10^3}{2\mathrm{N}}\frac{\Sigma_i N_i z_i^2}{V} = \tfrac{1}{2}\Sigma_i c_i z_i^2, \qquad (919, 1)$$

where $c_i$ is the concentration in gram-ions/litre, we obtain for water at 0° C., using $D = 88{\cdot}23$,

$$1-g = 0{\cdot}374 I^{\frac{1}{2}} \frac{\Sigma_i c_i z_i^2}{\Sigma_i c_i}\sigma\left(\frac{aI^{\frac{1}{2}}}{3{\cdot}08\times 10^{-8}}\right). \qquad (919, 2)$$

When all the cations have the same valency $z_+$ and all the anions the same valency $z_-$, the condition of electrical neutrality gives

$$z_+\Sigma_+ c_+ + z_-\Sigma_- c_- = 0. \qquad (919, 3)$$

By using (3) we can reduce (2) to

$$1-g = 0{\cdot}374 I^{\frac{1}{2}} z_+|z_-|\,\sigma\left(\frac{aI^{\frac{1}{2}}}{3{\cdot}08\times 10^{-8}}\right), \qquad (919, 4)$$

the form most convenient for application to a solution containing a single electrolyte.

Inserting numerical values into (918, 14), we obtain for water at 0° C., using $D = 88{\cdot}23$,

$$\log_{10}\gamma_{\pm} = -0{\cdot}486 z_+|z_-|\frac{I^{\frac{1}{2}}}{1+\left(\dfrac{a}{3{\cdot}08\times 10^{-8}}\right)I^{\frac{1}{2}}}. \qquad (919, 5)$$

For water at 25° C., using $D = 78{\cdot}54$, we have

$$\log_{10}\gamma_{\pm} = -0{\cdot}511 z_+|z_-|\frac{I^{\frac{1}{2}}}{1+\left(\dfrac{a}{3{\cdot}04\times 10^{-8}}\right)I^{\frac{1}{2}}}. \qquad (919, 6)$$

Owing to the fact that $D$ decreases as $T$ increases while only the product $DT$ occurs in the formulae, the numerical coefficients vary only slightly with temperature. For many purposes the round value 0·5, which is exact at 18° C., is sufficiently accurate in practice for temperatures between 0° C. and 25° C.

The most stringent test of these formulae would be by measurements at such high dilutions that the formulae become practically independent of $a$. This is unfortunately impossible in practice. For supposing $a \simeq 3\times 10^{-8}$ cm. and $I = 10^{-2}$, we have, according to Table 1, $\sigma(0{\cdot}1) = 0{\cdot}866$ which differs significantly from unity. Even at $I = 10^{-3}$ we have $\sigma = 0{\cdot}954$, so that in

practice the approximation $\sigma = 1$ is never accurate. The only possibility of testing the formulae is to examine whether they can be made to agree with experimental data with reasonable values of $a$.

Experimental values for $g$ are obtained most accurately by taking the ratio of the freezing-point depression of the solution to its value for an ideal solution of the same concentration. As the dilution increases the freezing-point depression decreases approximately in proportion to the concentration, and so the accuracy of $g$ varies inversely as the concentration. The relative accuracy of $1-g$ decreases still more rapidly. Instead of comparing observed and theoretical values of $g$ or $1-g$ it is therefore better to compare observed and theoretical values of the lowering of the freezing-point over a whole range of ionic strengths for an arbitrarily chosen value of $a$. The results of such a comparison may be summarized as follows: In practically all cases, where reliable freezing-point data are available for dilute aqueous solutions of strong electrolytes, there is agreement within the accuracy of the measurements between the observed and calculated freezing-point lowering *if the value assigned to a is suitably adjusted.* For example the data of Hovorka and Rodebush* agree with the theory with an accuracy of 0·0001° at all ionic strengths up to 0·01 if the values in Table 2 are assigned to $a$. These values of $a$ are of the right order of magnitude. The best data for some other electrolytes are fitted by assigning to $a$ values that are much smaller than the possible closest distance of approach of the ions—for instance 0·4 Å. for $KNO_3$† and 0·0 Å. for $KIO_3$.‡

TABLE 2

*Values of a, fitting Debye's values of g to Rodebush's measurements*

| Electrolyte | KCl | $CsNO_3$ | $K_2SO_4$ | $Ba(NO_3)_2$ | $MgSO_4$ | $CuSO_4$ | $La_2(SO_4)_3$ |
|---|---|---|---|---|---|---|---|
| $a$ in Å. | 3·8 | 3·0 | 3·0 | 2·1 | 3·0 | 2·2 | 3·0 |

Experimental values of $\gamma_\pm$ are obtained from measurements of either electromotive force or solubilities. In either case it is the ratio of values of $\gamma_\pm$ for a given electrolyte in solutions of varying composition that is determined directly. The assignment of absolute values to $\gamma_\pm$ always involves an extrapolation to infinite dilution where all $\gamma_\pm$ become unity. So effectively there are two adjustable parameters, one determined by the extrapolation, the other by the value of $a$. In the case of practically all reliable experi-

* Hovorka and Rodebush, *J. Am. Chem. Soc.* **47**, 1614 (1925) The values of $a$ actually given in this paper are computed incorrectly owing to a misprint in Debye and Huckel's table of values of $\sigma$. (Private communication.)

† Adams, *J. Am. Chem. Soc.* **37**, 481 (1915).

‡ Hall and Harkins, *J. Am. Chem. Soc.* **38**, 2658 (1916).

mental data, the adjustment of these two parameters can be made so as to give agreement between the observed and calculated values. The values of $a$ fitting the data are sometimes reasonable, but sometimes impossibly small, as for example in the solubility data of Brönsted and La Mer* which require $a = 0$ for many large complex ions. The true value for the closest distance of approach of two ions in a solution should be either very nearly the same as the mean of the ionic diameters determined in crystals, or greater if the ions are permanently hydrated. The true values cannot be less. It must be reluctantly admitted that the parameter $a$ is not a real mean ionic diameter, but rather a parameter correcting for a whole variety of theoretical imperfections. This is especially so for solutions containing small ions.

In solvents with smaller dielectric constants than water, still higher dilutions are required for the applicability of Debye's formulae. This fact and the experimental difficulty of obtaining the solvents pure considerably increase the difficulty of comparison between theory and experiment. It can, however, be said that the best experimental data at least do not disagree with the calculated values, but again the values that have to be assigned to $a$ appear to have no relation to the probable values of the ionic diameter.

**§ 920. Heat of dilution.** The heat of complete dilution $\Delta H$ of a given solution is defined as the heat *absorbed* when a large (effectively infinite) quantity of the pure solvent is added to the solution at constant temperature and pressure. If $H$ is the heat content for the original solution, $H_0$ for the pure solvent added, and $H_\infty$ for the resultant mixture, then the definition states that

$$\Delta H = H_\infty - (H + H_0). \tag{920, 1}$$

For an ideal solution, on the other hand, the heat contents are additive and $\Delta H$ is zero. If then we subtract from (1) the corresponding relation for the ideal values of the various quantities, we obtain

$$\Delta H = -H^{\text{el}} = T^2 \frac{\partial}{\partial T}\left(\frac{G^{\text{el}}}{T}\right), \tag{920, 2}$$

according to (917, 8). The operator $\partial/\partial T$ here denotes as usual $(\partial/\partial T)_{P,N}$. Consequently

$$\Delta H = -H^{\text{el}} = T^2\left[\left(\frac{\partial}{\partial T}\right)_{D,V,a} + \frac{\partial D}{\partial T}\left(\frac{\partial}{\partial D}\right)_{T,V,a} + \frac{\partial V}{\partial T}\left(\frac{\partial}{\partial V}\right)_{T,D,a} + \frac{\partial a}{\partial T}\left(\frac{\partial}{\partial a}\right)_{T,D,V}\right]\frac{G^{\text{el}}}{T}. \tag{920, 3}$$

* Brönsted and La Mer, *J. Am. Chem. Soc.* **46**, 555 (1924).

As nothing is known of $\partial a/\partial T$, we can evaluate (3) only for dilutions so great that $G^{el}$ is given by the limiting form

$$G^{el} = -\Sigma_i N_i z_i^2 \frac{|e|^2 \kappa}{3D}. \qquad (920, 4)$$

Combining (3) and (4) we obtain

$$\Delta H = -H^{el} = \Sigma_i N_i z_i^2 \frac{|e|^2 \kappa}{2D} \left\{ 1 + \frac{T}{D}\frac{\partial D}{\partial T} + \frac{1}{3}\frac{T}{V}\frac{\partial V}{\partial T} \right\}. \qquad (920, 5)$$

For a quantity of solution containing one mole of an electrolyte, whose molecule yields $q_+$ cations of valency $z_+$ and $q_-$ anions of valency $z_-$, (5) becomes

$$\Delta H = -H^{el} = \mathbf{N}(q_+ + q_-) z_+ |z_-| \frac{|e|^2 \kappa}{2D} \left\{ 1 + \frac{T}{D}\frac{\partial D}{\partial T} + \frac{1}{3}\frac{T}{V}\frac{\partial V}{\partial T} \right\}. \qquad (920, 6)$$

Inserting numerical values for aqueous solutions at 25° C., we obtain

$$\Delta H = -H^{el} = A\{\tfrac{1}{2}(q_+ + q_-) z_+ |z_-|\}^{\frac{3}{2}} c^{\frac{1}{2}}, \qquad (920, 7)$$

where $c$ is the concentration in moles/litre and $A$ is given by

$$A = 1{\cdot}37\left( 1 + \frac{T}{D}\frac{\partial D}{\partial T} + \frac{1}{3}\frac{T}{V}\frac{\partial V}{\partial T} \right) \text{Kcal./mole}. \qquad (920, 8)$$

Since for water at room temperatures $(T/D)\,\partial D/\partial T$ is roughly $-1{\cdot}4$, the greater part of this term is cancelled by the unit term. Thus $A$ is very sensitive to variations in the value assigned to $\partial D/\partial T$, which is not particularly well determined experimentally, so that $A$ cannot be fixed with an accuracy better than about 15 %. The term in $\partial V/\partial T$ has the value 0·025 in water at 25° C., and therefore introduces a reduction of about 6% in the positive value of $-A$. In Table 3 relevant values by various authors are given, arranged roughly in order of reliability.

At concentrations above tenth-molar the heats of dilution for various electrolytes in water are highly specific, being of either sign. The only accurate measurements at high dilutions are those of Lange and Robinson* and their collaborators. These are in good agreement with the theory and show for example that at high dilutions $H^{el} > 0$, so that on further dilution heat is evolved as required by (7) and (8). They show secondly a variation approximately proportional to the square root of the concentration. Thirdly, it is found that the limiting slope of the $(H^{el}, \sqrt{c})$-curves is determined primarily by the valency type of the electrolyte; being least for uni-univalent electrolytes, considerably greater for uni-bivalent, and greater still for bi-bivalent electrolytes. All this is in agreement with (7). The determination of the absolute value of this limiting slope is experimentally of extreme difficulty, owing to the great dilutions at which measurements are required

* Lange and Robinson, *Chem. Rev.* **9**, 89 (1931).

TABLE 3

*Observed values of the dielectric constant of water*

| 12·5° C. | | | 25° C. | | | | 40° C. | | | Authorities |
|---|---|---|---|---|---|---|---|---|---|---|
| $D$ | $\frac{\partial D}{\partial T}$ | $1+\frac{T}{D}\frac{\partial D}{\partial T}$ | $D$ | $\frac{\partial D}{\partial T}$ | $1+\frac{T}{D}\frac{\partial D}{\partial T}$ | $-A$ | $D$ | $\frac{\partial D}{\partial T}$ | $1+\frac{T}{D}\frac{\partial D}{\partial T}$ | |
| 83·16 | −0·379 | −0·301 | 78·54 | −0·361 | −0·371 | 0·48 | 73·28 | −0·341 | −0·457 | Wyman (1) |
| 83·29 | −0·393 | −0·347 | 78·57 | −0·362 | −0·374 | 0·48 | 73·41 | −0·326 | −0·390 | Drake, etc. (2) |
| 83·34 | −0·379 | −0·298 | 78·77 | −0·353 | −0·337 | 0·43 | 73·71 | −0·322 | −0·367 | Drude (3) |
| 82·77 | −0·368 | −0·269 | 78·26 | −0·349 | −0·329 | 0·42 | 73·18 | −0·330 | −0·411 | Drude (3) |
| 82·81 | −0·404 | −0·393 | 77·84 | −0·385 | −0·474 | 0·62 | 72·24 | −0·349 | −0·512 | Kockel (4) |
| 79·42 | −0·368 | −0·323 | 75·40 | −0·289 | −0·142 | 0·16 | 71·48 | −0·248 | −0·086 | Cuthbertson, etc. (5) |

*References to Table* 3

(1) Wyman, *Phys. Rev.* **35**, 623 (1930).
(2) Drake, Pierce and Dow, *Phys. Rev.* **35**, 613 (1930).
(3) Drude, *Wied. Ann.* **59**, 48 (1896). The first entry gives the figures derived by an interpolation formula; the second set were derived graphically.
(4) Kockel, *Ann. d. Phys.* **77**, 430 (1925).
(5) Cuthbertson and Maass, *J. Am. Chem. Soc.* **52**, 483 (1930).

for the limiting formulae independent of $a$ to be approximately valid. Moreover there is always an extrapolation involved since the quantity measured is the difference between $H^{el}$ at two finite concentrations. Thus no clear cut comparison can be made between the theory and experiment on this point even for uni-univalent electrolytes. It is fair to say, however, that within the uncertainty of the experimental data there is no inconsistency between the absolute value of this limiting slope in theory and experiment.

§ 921. **Critique of Debye's approximations.** The approximations and assumptions involved in Debye's treatment were not at all clearly formulated in the original presentation. They have subsequently been extensively analysed.* The most complete analysis is that of Kirkwood. His conclusions amplify and confirm those of Onsager. The analysis is too long to reproduce here and we shall content ourselves with a brief summary of the conclusions.

As we saw in § 910, the fundamental approximation of Debye is

$$W_{\alpha\beta} = z_\beta|e|\,\overline{{}^{\alpha}\psi(r)}, \qquad (921, 1)$$

which leads to the Poisson-Boltzmann equation. Since by definition

$$W_{\alpha\beta} = W_{\beta\alpha}, \qquad (921, 2)$$

* Kramers, *Proc. Sect. Sci. Amsterdam*, **30**, 145 (1927); Fowler, *Trans. Fara. Soc.* **23**, 434 (1927); Onsager, *Physikal. Zeit.* **28**, 277 (1927); *Chem. Rev.* **13**, 73 (1933); Kirkwood, *J. Chem. Phys.* **2**, 767 (1934).

this involves the assumption

$$\frac{{}^{\alpha}\overline{\psi(r)}}{z_\alpha} = \frac{{}^{\beta}\overline{\psi(r)}}{z_\beta}. \tag{921, 3}$$

Onsager has pointed out that these relations would hold exactly if the mean distribution of charge in the neighbourhood of a pair of ions $\alpha$ and $\beta$ at a distance $r$ from each other were always the sum of the charges induced by the two ions separately; because then the average forces acting on either ion in the given configuration would correspond to the average electric field at the distance $r$ from the other, the force from its own atmosphere vanishing by symmetry. For *low concentrations*, *small charges* and *large ionic diameters* (3) is very nearly fulfilled. Debye's approximate solution conforms to the condition (3). However, as soon as higher terms in the expansion of $e^{-z_\beta|e|{}^{\alpha}\overline{\psi(r)}/kT}$ become important, we can no longer expect the ionic atmospheres to be additive, and then Debye's assumption (1) becomes inaccurate.

From Kirkwood's analysis it appears that if the various average electric potentials such as ${}^{\alpha}\overline{\psi(r)}$, ${}^{\alpha\beta}\overline{\psi(r)}$ are expressible as power series in the charges, then the lowest terms will be identical with the values given by Debye's approximation. Now although it is physically impossible to decrease the charges of the ions below the value $|e|$, it is reasonable to expect that decreasing the concentrations will have an equivalent effect. In that case it seems almost certain that in the limit of high dilutions the true laws approach Debye's law. The extent of the inaccuracy due to Debye's approximations at finite concentrations still remains uncertain.

In the absence of any convincing theoretical argument or experimental evidence against the validity of Debye's approximation in the limit of high dilutions, it seems most reasonable to accept its validity as a limiting law, the accuracy of which increases with the dilution. In any case there exists no alternative treatment which could compete with Debye's.

The validity of Debye's limiting law (independent of ionic diameters) at high dilutions has also been confirmed by Kramers,* who examined the behaviour of the phase integral $\Omega$ in the limit of high dilutions by the mathematical device of replacing the ions by point charges with a superposed potential energy becoming infinite when any pair of ions are very close to each other and zero otherwise. The particular form assumed for this repulsive energy has no physical significance, but was introduced to make the phase integral converge. The limiting form at high dilutions is independent of the form so assumed for the repulsive energy, and confirms Debye's limiting formulae. Kramers' treatment gives no information concerning those formulae of Debye which involve the ionic diameter $a$.

* Kramers, *Proc. Sect. Sci. Amsterdam*, **30**, 145 (1927).

**§ 922. Güntelberg's evaluation of the ionic activity coefficients.** We recall that we evaluated $G^{el}$ as the electrical work of charging up all the ions simultaneously at the same relative rate. We then determined $\mu_i^{el}$ and $\gamma_i$ by the relation

$$kT \log \gamma_i = \mu_i^{el} = \partial G^{el}/\partial N_i. \tag{922, 1}$$

Accordingly we can define $\mu_i^{el}$ as the electrical work done when we add a single ion $i$ to the assembly. The value of $\mu_i^{el}$ should be unaffected if we replace the process of adding the ion $i$ to the assembly by the two imaginary steps

(*a*) adding the discharged ion $i$ to the assembly, the remaining ions having their full charges;

(*b*) gradually increasing the charge of $i$ from zero to $z_i$.

The electrical work in process (*a*) is due to the alteration in $V$ owing to the change of volume from $V$ to $V+V_i$; it is small compared to the work in process (*b*) and we shall neglect it. This is equivalent to omitting the second term in (918, 9).

The work in process (*b*) is easily evaluated since $\kappa$ remains effectively constant. Using (911, 10) we obtain

$$\mu_i^{el} = \int_0^{z_i} \psi_i |e|\, dz_i = -\int_0^{z_i} \frac{z_i|e|}{D} \frac{\kappa}{1+\kappa a} |e|\, dz_i$$

$$= -\frac{|e|^2\kappa}{D(1+\kappa a)} \int_0^{z_i} z_i\, dz_i = -\frac{z_i^2|e|^2\kappa}{2D(1+\kappa a)}, \tag{922, 2}$$

and consequently
$$\log \gamma_i = -\frac{z_i^2|e|^2}{2DkT} \frac{\kappa}{1+\kappa a}. \tag{922, 3}$$

This neat method of computing $\gamma_i$ is due to Guntelberg*. The fact that it leads to the same result as that obtained by first evaluating $G^{el}$, and then differentiating with respect to $N_i$, confirms the self-consistency of Debye's approximation with respect to the conditions (906, 12). We shall see that attempts to improve on Debye's approximation lead to solutions not self-consistent in this respect.

**§ 923. More accurate solutions of the Poisson-Boltzmann equation.** We mentioned that in certain cases agreement is reached between Debye's formulae and experimental data only by assigning values to $a$ considerably smaller than the true diameter of the ions. This can, in part at least, be ascribed to the inaccuracy of the approximation by which the Poisson-Boltzmann equation (910, 6) is replaced by (911, 2), an inaccuracy which matters so soon as $z|e|\,\psi(r)$ is comparable with $kT$. More accurate

* See Bjerrum, *Zeit. Physikal. Chem.* **119**, 145 (1926)

methods of solving the Poisson-Boltzmann equation have been developed, but they are necessarily rather elaborate.

For the sake of simplicity we shall restrict ourselves to the case where all the ions have the same numerical valency $z$. The Poisson-Boltzmann equation (910, 6) in this case reduces to

$$\frac{1}{r}\frac{d^2}{dr^2}\{r\psi(r)\} = \frac{8\pi|e|}{D} z \frac{N_\pm}{V} \sinh\frac{z|e|\,\psi(r)}{kT}, \qquad (923, 1)$$

where $N_\pm$ is the number of ions of either sign in the assembly. The solution of this equation is required for which $\psi \to 0$ and $\partial\psi/\partial r \to 0$ as $r \to \infty$, and

$$\frac{\partial\psi}{\partial r} \to \mp \frac{z|e|}{Da^2} \quad (r \to a). \qquad (923, 2)$$

It is convenient to introduce the notation

$$\kappa = +\left(\frac{8\pi|e|^2}{DkT} z^2 \frac{N_\pm}{V}\right)^{\frac{1}{2}}, \quad \rho = \kappa r, \quad x = \kappa a, \quad y = \frac{z|e|\,\psi}{kT}, \quad b = \frac{z^2|e|^2}{DkTa}. \qquad (923, 3)$$

Then
$$\frac{1}{\rho}\frac{d^2}{d\rho^2}(\rho y) = \sinh y, \qquad (923, 4)$$

with the boundary conditions

$$y \to 0, \quad dy/d\rho \to 0 \quad (\rho \to \infty), \qquad (923, 5)$$

$$\frac{dy}{d\rho} = -\frac{b}{x} \quad (\rho = x). \qquad (923, 6)$$

Debye's approximation consists in replacing $\sinh y$ by $y$.

There is no difficulty in principle in obtaining the desired solution without this approximation. It has been achieved in an elementary way by Müller,* who used the approximation $\sinh y = y$ only for sufficiently large values of $\rho$. For such values of $\rho$ Debye's solution

$$y(\rho) = A\rho^{-1}e^{-\rho} \qquad (923, 7)$$

is valid, but when $\rho$ becomes smaller $y(\rho)$ deviates from (7) and the value of $A$ cannot be determined from the boundary condition at $\rho = x$. Müller therefore continued (4) inwards by numerical integration to $\rho = x$, determined $A$ to fit the boundary condition, and so finally found $y(x)$ as a function of $b$ and $x$.

An alternative solution has been given by Gronwall, La Mer and Sandved.† They assume a solution in the form of a power series in $(z^2|e|^2/DkTa)$ and by successive approximations evaluate the coefficients as functions of $\kappa a$.

* Müller, *Physikal. Zeit.* **28**, 324 (1927).

† Gronwall, La Mer and Sandved, *Physikal. Zeit.* **29**, 358 (1928).

The result has the form

$$\pm\frac{z|e|\psi}{kT}=\frac{z^2|e|^2}{DkTa(1+\kappa a)}+\sum_{s=1}^{\infty}\left(\frac{z^2|e|^2}{DkTa}\right)^{2s+1}y_{2s+1}(\kappa a), \quad (923, 8)$$

where the $y_{2s+1}(\kappa a)$ are determinable functions of $\kappa a$. When we subtract the self potential, this gives

$$\pm\frac{z|e|\psi_\alpha}{kT}=\frac{z^2|e|^2}{DkT}\frac{\kappa}{1+\kappa a}+\sum_{s=1}^{\infty}\left(\frac{z^2|e|^2}{DkTa}\right)^{2s+1}y_{2s+1}(\kappa a). \quad (923, 9)$$

From either of these solutions for $\psi_\alpha$, whether that of Müller, or that of Gronwall, La Mer and Sandved, we can by straightforward application of (917, 2) evaluate $G^{el}$, as in § 913, and can then derive the osmotic coefficient or the activity coefficient of the electrolyte by straightforward thermodynamics.

If the solution either of Müller or of Gronwall, La Mer and Sandved is applied to the experimental data, more reasonable values are obtained for $a$ than those of Debye's solution. In fact Gronwall has shown that, if the values of $a$ derived from his formula are denoted by $a_G$ and those derived from Debye's by $a_D$, then $a_G$ remains positive even if $a_D \to -\infty$.

We shall, however, not go further into the details of these solutions of the Poisson-Boltzmann equation because they are not self-consistent. The simplest way to show this is to calculate $\mu_i^{el}$ first by differentiation of $G^{el}$ and then by Guntelberg's method. The processes do not lead to the same value and therefore neither can be exact. This means that the integrability conditions (906, 12) are not satisfied. Owing to the special symmetry of the particular assembly considered, the other condition (910, 4),

$$\frac{\psi_\alpha}{z_\alpha}=\frac{\psi_\beta}{z_\beta}, \quad (923, 10)$$

is here automatically satisfied.

In the more general case of ions of differing numerical valencies it is apparent at once that the $\overline{{}^\alpha\psi(r)}$ depend on the $N_\beta$ and $z_\beta$ not solely through the combination $\Sigma_i N_i z_i^2$ which occurs in $\kappa$, but through other combinations $\Sigma_i N_i z_i^{2+r}$ ($r$ integral) as well. The conditions of self-consistency then inevitably fail far more completely than in the symmetrical case. It must be regretfully admitted that this most promising method of evaluating $\Omega(T)$ cannot be carried *logically* beyond the first approximation of Debye.

**§ 924. Bjerrum's treatment of ion association.** We have seen that attempts to improve on Debye's theory by solving more accurately the Poisson-Boltzmann equation are in general doomed to failure, because

this equation ceases to be self-consistent. Debye's approximation is itself valid when both

$$\frac{|z_\alpha z_\beta|\,|e|^2\kappa}{DkT} \ll 1. \qquad (924,1)$$

$$\frac{|z_\alpha z_\beta|\,|e|^2}{DkTa} \ll 1. \qquad (924,2)$$

The second condition is independent of the concentration, and it is this restriction to large ions which we have still to find a general means of avoiding.

An entirely different method of avoiding this restriction has been proposed by Bjerrum.* Though at first sight less elegant and more arbitrary than attempts to solve the Poisson-Boltzmann equation more accurately, it has the important advantage of being self-consistent. The principle and application of Bjerrum's method is simple, so long as all ions have the same numerical valency $z$, and we shall confine our attention to this case.

It is clear that the length

$$q = \frac{|z_\alpha z_\beta|\,|e|^2}{2DkT} = \frac{z^2|e|^2}{2DkT} \qquad (924,3)$$

is a critical radius in any theory, for if $a \gg q$ then Debye's theory applies in its original form. We imagine therefore the centre of every ion surrounded by a sphere of radius $q$. For each ion there are then the following alternatives: there may be (i) no other ion, (ii) one other ion of opposite charge, (iii) one other ion of the same charge, or (iv) more than one other ion, inside the spherical shell $r = q$. The relative frequency of these arrangements can easily be evaluated approximately, for in calculating distributions in which one ion (or a few ions) is within a certain small region immediately round the central ion the screening effect of the other (distant) ions may be ignored. The potential due to the central ion at a distance $r$ can therefore be given the simple value $\pm z|e|/Dr$. The average number of ions of the opposite or the same charge within the sphere $r = q$ is therefore

$$\frac{N_\mp}{V}\int_a^q e^{\pm z^2 e^2/DkTr}\,4\pi r^2\,dr, \qquad (924,4)$$

the $+$ sign referring to ions of opposite and the $-$ to ions of the same charge. For sufficiently small values of $N_\pm$ this number is small compared with unity even for the $+$ sign and still smaller for the negative sign. We may then say that we have effectively a fraction $\alpha$ ($\alpha \ll 1$) of ions with an ion of the opposite sign within the sphere $r = q$, and a negligible fraction with an ion of the same sign. The fraction with two ions within $r = q$ can easily be seen to be of order at most $\alpha^2$ and may therefore also be neglected. The remaining

* Bjerrum, *Kgl Danske Vid. Selsk., Math-fys Medd.* **7**, no. 9 (1926).

fraction $1-\alpha$ has no other ion within $r = q$. Of the four possible arrangements only (i) and (ii) are effectively present.

The novel idea in Bjerrum's treatment is to deal with these two classes of ions separately. The fraction $\alpha$ is called *associated ion pairs* and the fraction $1-\alpha$ free or unassociated ions. Bjerrum's approximation is now to ignore the effect of the electrostatic field of an associated pair on the remaining ions and to apply Debye's theory to the free ions, assuming of course that they have an effective diameter $q$, for if they come closer than $q$ they cease to count as free.

For sufficiently small concentrations we have shown that

$$\alpha = \frac{N_{\pm}}{V}\int_a^q e^{z^2|e|^2/DkTr}\,4\pi r^2\,dr. \qquad (924, 5)$$

To obtain formulae for values of $\alpha$ for which the condition $\alpha \ll 1$ fails, we can calculate $\alpha$ by treating the distribution as one of dissociative equilibrium between the associated ion pairs and the free ions. The condition of dissociative equilibrium takes the form

$$\frac{(1-\alpha)^2 N_{\pm}}{\alpha} = \frac{f_i f_j}{f_{ij}}, \qquad (924, 6)$$

where $f_i$, $f_j$ and $f_{ij}$ are the partition functions for the free ions and the associated pair respectively. Only the configurational factors can contribute to this ratio, and it can be shown that

$$\frac{f_i f_j}{f_{ij}} = \frac{V}{\int_a^q e^{z^2|e|^2/DkTr}\,4\pi r^2\,dr}, \qquad (924, 7)$$

if the electrostatic forces due to the distant ions are ignored. To this approximation therefore

$$\frac{(1-\alpha)^2}{\alpha}\frac{N_{\pm}}{V} = K = \left[\int_a^q e^{z^2|e|^2/DkTr}\,4\pi r^2\,dr\right]^{-1}. \qquad (924, 8)$$

To the next approximation

$$\frac{(1-\alpha)^2}{\alpha}\frac{N_{\pm}}{V} = K\gamma_z'^2, \qquad (924, 9)$$

where $\gamma_z'$ is the calculated activity coefficient of a free ion of valency $\pm z$, the activity coefficient of the associated ion pair being taken as unity. The value of $\gamma_z'$ is given by Debye's formula

$$\log \gamma_z' = -\frac{z^2|e|^2}{DkT}\frac{\kappa}{1+\kappa q}, \qquad (924, 10)$$

but with $\kappa$ determined by the concentration of free ions, that is

$$\kappa = +\left\{\frac{8\pi N_{\pm}(1-\alpha)z^2|e|^2}{DkTV}\right\}^{\frac{1}{2}}. \qquad (924, 11)$$

Since $\gamma_z'$ in (9) then depends on $\alpha$, (9) has to be solved by successive approximation. The values of $\alpha$ computed by Bjerrum for univalent ions in water at 18° C. are given in Table 4.

TABLE 4

*Degree of association $\alpha$ of univalent ions in water at* 18° C.

| $a \times 10^8$ cm. | 2·82 | 2·35 | 1·76 | 1·01 | 0·70 | 0·47 |
|---|---|---|---|---|---|---|
| $q/a$ | 2·5 | 3 | 4 | 7 | 10 | 15 |
| $c$ in moles per litre | | | | | | |
| 0·0001 | — | — | — | — | 0·001 | 0·027 |
| 0·0002 | — | — | — | — | 0·002 | 0·049 |
| 0·0005 | — | — | — | 0·002 | 0·006 | 0 106 |
| 0·001 | — | 0·001 | 0·001 | 0·004 | 0·011 | 0 177 |
| 0·002 | 0·002 | 0·002 | 0·003 | 0·007 | 0·021 | 0·274 |
| 0·005 | 0·002 | 0·004 | 0·007 | 0·016 | 0·048 | 0·418 |
| 0·01 | 0·005 | 0·008 | 0·012 | 0·030 | 0·083 | 0 529 |
| 0·02 | 0·008 | 0·013 | 0·022 | 0·053 | 0·137 | 0 632 |
| 0·05 | 0·017 | 0·028 | 0·046 | 0·105 | 0·240 | 0·741 |
| 0·1 | 0·029 | 0·048 | 0·072 | 0·163 | 0·336 | 0·804 |
| 0·2 | 0·048 | 0·079 | 0·121 | 0·240 | 0·437 | 0·854 |

Once $\alpha$ is determined substitution in (10) gives $\gamma_z'$ the calculated activity coefficient $\gamma_z'$ of a *free* ion. The mean activity coefficient $\gamma_{\pm}$ of the electrolyte is then obtained from

$$\gamma_{\pm} = (1-\alpha)\gamma_z', \qquad (924, 12)$$

a relation which expresses the fact that the partial potential averaged for all ions, free or associated, must be equal to the partial potential of the free ions The osmotic coefficient $g$ can then be calculated from the thermodynamic relation

$$d\{(1-g)c\} = c\,d\log\gamma_{\pm}. \qquad (924, 13)$$

The calculations have been carried through by Bjerrum.

The results for uni-univalent ions can easily be transformed to apply to other valencies and other solvents by making use of the fact that the osmotic coefficient $g$ depends only on the ratios $q : a : c^{-\frac{1}{2}}$, or is a function only of $cz^6|e|^6/(DkT)^3$ and $z^2|e|^2/(DkTa)$.

By comparing the values of $g$ obtained from freezing-point measurements with calculated values much more reasonable values of $a$ are obtained than from the simple theory, especially for bi-bivalent electrolytes, and for uni-univalent electrolytes in solvents of lower dielectric constant such as the alcohols.

**§ 925. The choice of $q$.** Before leaving this subject it is proper to enquire why precisely the distance $q$ should have been taken arbitrarily as the critical radius distinguishing between free and associated ions. The answer is that the exact value of $q$ is unimportant, and that the final result is not greatly different if we replace $q$ by e.g. $\frac{1}{2}q$ or $2q$. A revised form of the theory due to Fuoss* makes this point clearer by virtually eliminating the arbitrary choice of $q$.

In Fuoss's treatment *every* ion is paired with some one ion of the opposite sign according to the following convention. *A positive ion and a negative ion, the centre of which lies at a distance between $r$ and $r+dr$ from the positive ion, are defined to be an ion pair provided that no other unpaired negative ion lies within a sphere of radius $r$ drawn round the positive ion.* Let the centre of a particular positive ion be taken as origin and let $G(r)\,dr$ be the probability that this ion forms a pair with one of the $N$ negative ions at a distance between $r$ and $r+dr$, there being no unpaired negative ion nearer than a distance $r$. We may then assert that $G(r)$ will be proportional to $N$; to $4\pi r^2 dr/V$; to the Boltzmann factor $e^{z^2|e|^2/DrkT}$ (this neglects screening); and finally to the probability $f(r)$ that an unpaired negative ion is not already present in the volume $\frac{4}{3}\pi r^3$. The probability that the first unpaired negative ion is present in the spherical shell $x<r<x+dx$ is by definition $G(x)\,dx$ and therefore the probability $f(r)$ that no such ion is anywhere present in the sphere of volume $\frac{4}{3}\pi r^3$ is

$$f(r) = 1-\int_a^r G(x)\,dx. \tag{925, 1}$$

Combining these statements we see that we have asserted that

$$G(r)\,dr = \frac{4\pi N}{V}\,r^2\,dr\,e^{2q/r}\left\{1-\int_a^r G(x)\,dx\right\}. \tag{925, 2}$$

For small $r$ the probability $G(r)\,dr$ must reduce to the ordinary average number of ions of opposite sign, that is to

$$G(r) \sim \frac{4\pi N}{V}\,r^2 e^{2q/r}. \tag{925, 3}$$

With this boundary condition equation (2) can be solved giving

$$G(r) = \frac{4\pi N}{V}\,r^2 \exp\left\{\frac{2q}{r}-\frac{4\pi N}{V}\int_a^r x^2 e^{2q/x}\,dx\right\}. \tag{925, 4}$$

It can be verified that

$$\int_a^{V^{\frac{1}{3}}} G(r)\,dr \simeq \int_a^{\infty} G(r)\,dr = 1. \tag{925, 5}$$

* Fuoss, *Trans. Fara. Soc.* **30**, 967 (1934).

We now study the dependence of $G(r)$ on $r$. We see that $G(r)$ has stationary values when

$$\frac{2}{r} - \frac{2q}{r^2} - \frac{4\pi N}{V} r^2 e^{2q/r} = 0. \tag{925, 6}$$

There is always one maximum value, and there is also a minimum if $q > a$. If the concentration is fairly small so that $q \ll (V/N)^{\frac{1}{3}}$, and if also $q > a$, then the minimum occurs at

$$r = q\left(1 + \frac{4\pi N}{V}\frac{e^2}{2} q^3 + \dots\right), \tag{925, 7}$$

or at $r \simeq q$, and the maximum at

$$r = (V/2\pi N)^{\frac{1}{3}}\{1 - 2q(V/2\pi N)^{-\frac{1}{3}} + \dots\}, \tag{925, 8}$$

or at $r \simeq (V/2\pi N)^{\frac{1}{3}} = \rho$. These give

$$G_{\min} \simeq G(q) \simeq \frac{4\pi N}{V} e^2 q^2, \tag{925, 9}$$

$$G_{\max} \simeq G(\rho) \simeq \left(\frac{16\pi N}{e^2 V}\right)^{\frac{1}{3}}, \tag{925, 10}$$

while for ions in contact

$$G(a) \simeq \frac{4\pi N}{V} a^2 e^{2q/a}. \tag{925, 11}$$

It is thus approximately true that $G(a) \propto N/V$, while $G(\rho) \propto (N/V)^{\frac{1}{3}}$, so that at low concentrations $G(\rho) \gg G(a)$ while at high the order will be reversed. For given solvent, temperature, valency, and ionic diameter there will be a concentration for which these two probabilities are equal. This concentration $c_0$ has the value $97 e^{-3q/a}/(10^8 a)^3$. If for example we take $T = 300°$ K., $a = 4{\cdot}6$ Å., then $\log_{10} c_0 = -78{\cdot}7 z^2/D$. Thus for aqueous solutions of a bi-bivalent electrolyte the critical concentration is about ten thousandth molar. An example of $G(r)$ is shown in Fig. 1 for this case. The various characteristic distances in Å. are $a = 4{\cdot}6$, $(V/2N)^{\frac{1}{3}} = 202$, $1/\kappa = 153$, $q = 14$, $\rho = 138$, and their variations as $c$ changes can be derived from the foregoing formulae. The maximum at $E$ and the inflexions at $D$ and $F$ move, however, only at rates proportional to $c^{\frac{1}{3}}$ both vertically and horizontally, while $A$ and $C$ move upwards at rates proportional to $c$. It follows that over a wide range of values of $c$ there are very few ion pairs at $C$ in the neighbourhood of $r \simeq q$ compared with those round $A$ or $E$ or both. It is therefore legitimate to divide the ion pairs up into these two classes by an arbitrary convention provided that the dividing radius is chosen near $q$ as Bjerrum has done. It is clearly then the correct first approximation to treat the two distinct classes as contributing to the electrical energy according to Debye's

theory for the distant pairs, while giving zero for the associated pairs. There is therefore no ground for the assertion of Gronwall, La Mer and Sandved* that Bjerrum's assumptions are arbitrary.

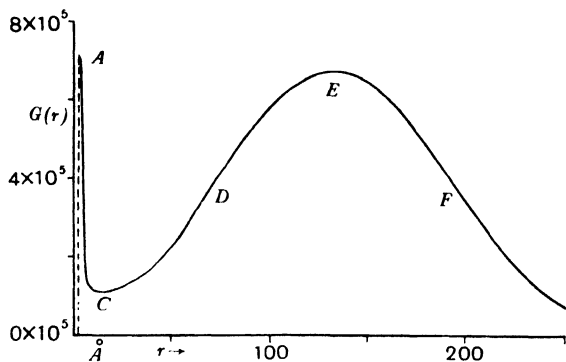



Fig. 1. The distribution function $G(r)$ as a function of $r$.

**§ 926. Specific interaction of ions.** The most valuable contribution of Debye's theory consists of the limiting laws for high dilutions, which do not involve the ionic diameter. The formulae involving the mean ionic diameter $a$ may be fairly satisfactory if $a$ is not too small. When $a$ is small they fail, and the variations, such as those of Bjerrum and of Gronwall, which attempt to correct for this failure are all cumbersome and none of them exact. Moreover the treatment of the ions as rigid spheres is far too crude to take account of the specific properties of various ions of the same valency, for the ions differ not merely in size but also in shape and polarizability, all of which factors have to be represented by a change of $a$ in this theory and its extensions. It is an obvious suggestion for improvement that in a solution containing several kinds of ions independent values of $a$ should be assigned to each ion pair. It would be necessary, however, to ensure that the partial potentials of the various kinds of ions satisfy the thermodynamic relationships

$$\frac{\partial \mu_i^{\text{el}}}{\partial N_j} = \frac{\partial \mu_j^{\text{el}}}{\partial N_i}, \tag{926, 1}$$

and any simplification of the calculation would be liable to fail to preserve these necessary relationships.

Anything like a complete calculation being at present apparently out of the question, an attempt has been made† to solve the simpler problem;

* Gronwall, La Mer and Sandved, *Physikal. Zeit.* **29**, 358 (1928).

† Guggenheim, *Proc. 18th Scandinavian Scientific Congress, Copenhagen* (1929); *Phil. Mag.* **19**, 588 (1935), which includes a review of the conditions for the validity of Debye's theory and the various attempts to improve on it.

***Given the equilibrium properties of dilute solutions of each single electrolyte, to calculate the specific equilibrium properties of a solution containing several such electrolytes.*** A standard of comparison is required to which we can refer the properties of any actual solution of electrolytes. Among a variety of possible standards the most convenient seems to be an imaginary electrolyte containing a mixture of ions of the same concentrations and valencies as those of the actual electrolyte, which accurately obeys Debye's formulae for a definite value of the parameter $a$. For numerical convenience we choose for $a$ the value 3·08 Å. which makes $\kappa a$ equal to $I^{\frac{1}{2}}$.

Let us now consider two actual ions, $\alpha$ and $\beta$, in a given relative configuration. Their mutual potential energy $W_{\alpha\beta}$ as defined in § 908 can be regarded as the sum of the two terms

$$W_{\alpha\beta} = W_{\alpha\beta}^{\text{sta}} + W_{\alpha\beta}^{\text{spe}}, \tag{926, 2}$$

where $W_{\alpha\beta}^{\text{sta}}$ is the value for the two standard ions of the corresponding valencies, and $W_{\alpha\beta}^{\text{spe}}$ measures the specific deviations of the interaction of the given ion pairs from that of the corresponding standard ion pair. For all except small distances $W_{\alpha\beta}^{\text{sta}}$ is effectively the Coulomb energy, while $W_{\alpha\beta}^{\text{spe}}$ is negligible except at very small distances. We shall now make the assumption that the contribution of $W_{\alpha\beta}^{\text{spe}}$ to the thermodynamic functions can be added as a correction additional to the electrostatic terms arising from $W_{\alpha\beta}^{\text{sta}}$. This assumption cannot be accurate, but we may expect it to be a reasonable approximation so long as the contribution is small compared with the electrostatic terms. We then write $G^{\text{el}}$ as before for the contribution of the interionic potentials to $G$, and may break this up into

$$G^{\text{el}} = G^{\text{sta}} + G^{\text{spe}}, \tag{926, 3}$$

$G^{\text{sta}}$ being given by (917, 3) for the chosen $a$, while $G^{\text{spe}}$ is an additive term vanishing when $W_{\alpha\beta}^{\text{spe}} = 0$. Now this additive term arises from effectively short-range forces, and may therefore be evaluated as a contribution to $\log \Omega(T)$ by the methods of Chapter VII for imperfect gases. The arguments there used must be generalized, so that the standard value of $\Omega(T)$ contains the standard interionic energies $W_{\alpha\beta}^{\text{sta}}$. In Chapter VII we found an extra contribution to the free energy of

$$\frac{kT}{V}\int (1 - e^{-W_{\alpha\beta}/kT})\, d\omega \tag{926, 4}$$

per molecule pair, the integrand being effectively non-zero over a short range only. Here the extra contribution can be shown to be, to the same approximation,

$$\frac{kT}{V}\int e^{-W_{\alpha\beta}^{\text{sta}}/kT}(1 - e^{-W_{\alpha\beta}^{\text{spe}}/kT})\, d\omega \tag{926, 5}$$

per ion pair. The expression (5) is strictly $F^{spe}$, calculated by establishing the $W^{spe}_{\alpha\beta}$ at constant temperature and volume. For reasons similar to those given in § 917 it is, however, probably more accurate to take it as equal to $G^{spe}$. We thus obtain the following expression

$$G^{el} = G^{sta} + G^{spe}$$
$$= -\frac{|e|^2\kappa}{3D}\Sigma_i N_i z_i^2 \tau(\kappa a) + \frac{kT}{V}\Sigma_{ij}\frac{N_i N_j}{\sigma_{ij}}\int e^{-W^{sta}_{ij}/kT}(1-e^{-W^{spe}_{ij}/kT})\,d\omega. \quad (926,6)$$

Not all the specific terms are equally important; the terms arising from pairs of ions of the same sign for which $W^{sta}_{ij} > 0$ will be small compared with those arising from pairs of ions of opposite sign for which $W^{sta}_{ij} < 0$.* We may therefore simplify $G^{el}$ to the expression

$$G^{el} = -\frac{|e|^2\kappa}{3D}\Sigma_i N_i z_i^2 \tau(\kappa a) + \frac{kT}{V}\Sigma_{R,X} N_R N_X \upsilon_{R,X}, \quad (926,7)$$

where $R$ is any cation and $X$ any anion, and $\upsilon_{R,X}$ is a coefficient depending only on the temperature and the solvent, but specific to the pair of ions in question. These $\upsilon_{R,X}$'s may each be determined by the properties of a single electrolyte, and the equilibrium properties of a general mixed electrolyte will then be derivable from (7).

The specific contribution $\mu^{spe}_{H_2O}$ to the partial potential of the solvent water will be given by

$$\mu^{spe}_{H_2O} = \frac{\partial G^{spe}}{\partial N_{H_2O}} = V_{H_2O}\frac{\partial G^{spe}}{\partial V} = -kT\,V_{H_2O}\Sigma_{R,X}\frac{N_R}{V}\frac{N_X}{V}\upsilon_{R,X}. \quad (926,8)$$

Provided the solution is extremely dilute, the corresponding contribution to $1-g$ is

$$\frac{\mu^{spe}_{H_2O}}{kT\,V_{H_2O}\Sigma_i N_i/V} = -\frac{\Sigma_{R,X} N_R N_X/V^2}{\Sigma_R N_R/V + \Sigma_X N_X/V}\upsilon_{R,X}$$
$$= -\frac{2\Sigma_{R,X} c_R c_X}{\Sigma_R c_R + \Sigma_X c_X}\beta_{R,X}, \quad (926,9)$$

where $c_R$, $c_X$ denote concentrations in gram-ions/litre and the $\beta_{R,X}$ are related to the $\upsilon_{R,X}$ by

$$\beta_{R,X} = \frac{1}{2}\frac{\mathbf{N}}{10^3}\upsilon_{R,X}. \quad (926,10)$$

For the sake of brevity we shall confine our further discussion to solutions containing electrolytes all of the same valency type, such that each molecule yields $q_+$ cations of valency $z_+$ and $q_-$ anions of valency $z_-$. If then $c$ denotes the total concentration of electrolyte in moles/litre, we have

$$c = \Sigma_R c_R/q_+ + \Sigma_X c_X/q_-. \quad (926,11)$$

* Cf. Brönsted, *J. Am. Chem. Soc.* **44**, 877 (1922). His formulation of the *principle of specific interaction* states that: "Ions are uniformly influenced by ions of their own sign and specifically influenced only by ions of the opposite sign."

Let the composition of the solution be defined by the fractions $x_R = c_R/\Sigma_R c_R, \ldots$ of all the cations that are of the type $R$ and the fractions $x_X/\Sigma_X x_X, \ldots$ of all the anions that are of the type $X$. Then (9) can be rewritten as

$$\bar{q}c\Sigma_{R,X}\, x_R x_X \beta_{R,X}, \qquad (926, 12)$$

where $q$ is defined by

$$\frac{2}{q} = \frac{1}{q_+} + \frac{1}{q_-}, \qquad (926, 13)$$

being unity for symmetrical electrolytes.

Using (919, 4) with $a$ chosen equal to 3·08 Å. for the standard contribution to $(1-g)$, we obtain as the complete formula for $1-g$

$$1-g = 0{\cdot}374z_+|z_-|\, I^{\frac{1}{2}}\sigma(I^{\frac{1}{2}}) - \bar{q}c\Sigma_{R,X}\, x_R x_X \beta_{R,X}. \qquad (926, 14)$$

For a single electrolyte this reduces to

$$1-g = 0{\cdot}374z_+|z_-|\, I^{\frac{1}{2}}\sigma(I^{\frac{1}{2}}) - \bar{q}c\beta_{R,X}. \qquad (926, 15)$$

The corresponding formula for the mean activity coefficient of an electrolyte consisting of the ions $R, X$ in a mixture of electrolytes of the same valency type is at 20° C.

$$\log_{10}\gamma_{R,X} = -\frac{0{\cdot}500z_+|z_-|\, I^{\frac{1}{2}}}{1+I^{\frac{1}{2}}} + \frac{qc}{2{\cdot}30}\{\Sigma_{X'}\, x_{X'}\beta_{R,X'} + \Sigma_{R'}\, x_{R'}\beta_{R',X}\}. \qquad (926, 16)$$

For a solution of a single electrolyte this reduces to

$$\log_{10}\gamma_{R,X} = -\frac{0{\cdot}500z_+|z_-|\, I^{\frac{1}{2}}}{1+I^{\frac{1}{2}}} + \frac{2q}{2{\cdot}30}c\beta_{R,X}. \qquad (926, 17)$$

There is excellent agreement between the best freezing-point data and (15) for single electrolytes of various valency types. The values of $\beta_{R,X}$ which best fit the data are given in Table 5. With these values the disagreement between calculated and observed freezing-points is probably less than the experimental error for all ionic strengths up to 0·1. At higher ionic strengths the formulae are not reliable. The dependence of $1-g$ on the ionic strength is shown by the curves in Fig. 2, where $(1-g)/z_+|z_-|$ is plotted against $I^{\frac{1}{2}}$. Fig. 3 shows the corresponding behaviour of the mean activity coefficients $\gamma_{R,X}$ calculated according to (17) with the same $\beta_{R,X}$ values.

Such data as are available for mixed electrolytes are mostly in excellent agreement with the theory.* It would take too much space to discuss these here. We would only point out that for a mixture of electrolytes of the same valency type at a given total concentration the osmotic coefficient is according to (14) in general a quadratic function of the fractions $x_R$, $x_X$ describing the composition of the solution. Only in the special case where

* For further details see: Bronsted, *J. Am. Chem. Soc.* **44**, 877 (1922); Guntelberg, *Zeit. Physikal. Chem.* **123**, 199 (1926); Guggenheim, *Phil Mag.* **19**, 588 (1935); **22**, 322 (1936); Guntelberg, *Studier over Elektrolyt-Activiteter* (Copenhagen, 1938).

TABLE 5

*Values of β fitting freezing-point data of single electrolytes*

| Electrolyte | $\bar{q}$ | $\beta$ | $\bar{q}\beta$ | Authority |
|---|---|---|---|---|
| HCl | 1 | 0·275 | — | (4) |
| LiCl | 1 | 0·223 | — | (8) |
| NaCl | 1 | 0·135 | — | (3), (8) |
| KCl | 1 | {0·065 | — | (8) |
| | | {0·083 | — | (1), (5) |
| TlCl | 1 | 0·40 | — | (4) |
| $LiClO_3$ | 1 | 0·280 | — | (7) |
| $NaClO_3$ | 1 | 0·040 | — | (7) |
| $KClO_3$ | 1 | −0·165 | — | (7) |
| $LiClO_4$ | 1 | 0·380 | — | (7) |
| $NaClO_4$ | 1 | 0·075 | — | (7) |
| $KClO_4$ | 1 | −0·500 | — | (7) |
| $LiNO_3$ | 1 | 0·260 | — | (7) |
| $NaNO_3$ | 1 | 0·000 | — | (7) |
| $KNO_3$ | 1 | {−0·237 | — | (7) |
| | | {−0·29 | — | (1) |
| $CsNO_3$ | 1 | 0·00 | — | (5) |
| $NaIO_3$ | 1 | −0·40 | — | (2) |
| $KIO_3$ | 1 | −0·40 | — | (2) |
| $LiO_2CH$ | 1 | 0·140 | — | (8) |
| $NaO_2CH$ | 1 | 0·170 | — | (8) |
| $KO_2CH$ | 1 | 0·190 | — | (8) |
| $LiO_2C.CH_3$ | 1 | 0·210 | — | (8) |
| $NaO_2C.CH_3$ | 1 | 0·290 | — | (8) |
| $KO_2C.CH_3$ | 1 | 0·290 | — | (8) |
| $Na_2SO_4$ | $\frac{4}{3}$ | −0·45 | −0·60 | (6) |
| $K_2SO_4$ | $\frac{4}{3}$ | 0·00 | 0·00 | (2), (5) |
| $Ba(NO_3)_2$ | $\frac{4}{3}$ | −0·41 | −0·55 | (6), (5) |
| $MgSO_4$ | 1 | 0·00 | 0·00 | (2), (5) |
| $CuSO_4$ | 1 | −1·7 | −1·7 | (5) |
| $La(NO_3)_3$ | $\frac{3}{2}$ | 2·6 | +3·9 | (2) |
| $La_2(SO_4)_3$ | $\frac{12}{5}$ | 0·00 | 0·00 | (5) |

*References to Table 5*


(1) Adams, *J. Am. Chem. Soc.* **37**, 481 (1915).
(2) Hall and Harkins, *J. Am. Chem. Soc.* **38**, 2658 (1916).
(3) Harkins and Roberts, *J. Am. Chem. Soc.* **38**, 2676 (1916).
(4) Randall and Vanselow, *J. Am. Chem. Soc.* **46**, 2418 (1924).
(5) Hovorka and Rodebush, *J. Am. Chem. Soc.* **47**, 1614 (1925).
(6) Randall and Scott, *J. Am. Chem. Soc.* **49**, 647 (1927).
(7) Scatchard, Jones and Prentiss, *J. Am. Chem. Soc.* **54**, 2690 (1932), **56**, 805 (1934).
(8) Scatchard and Prentiss, *J. Am. Chem. Soc* **54**, 2696 (1932); **55**, 4355 (1933); **56**, 807 (1934).


there is only one type of anion $X$ (and of course in the analogous case of only one type of cation) (14) reduces to

$$1-g = 0{\cdot}374z_+|z_-|\, I^{\frac{1}{2}}\sigma(I^{\frac{1}{2}}) - \bar{q}c\Sigma_R x_R \beta_{R,X}, \qquad (926, 18)$$

which is linear* in the fractions $x_R$.

* See Guntelberg, *Zeit. Physikal. Chem.* **123**, 236 (1926).

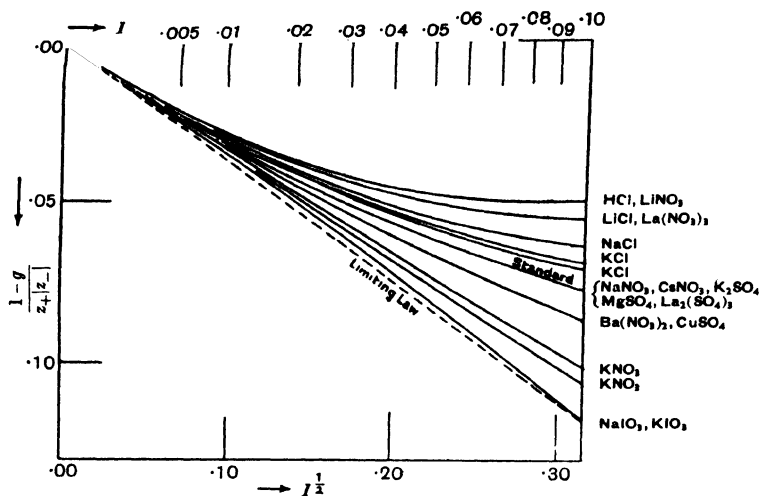



Fig. 2. Osmotic coefficients for solutions of various electrolytes. Curves drawn according to (15) for the best values of $\beta$, given in Table 5, in good agreement with the observations.

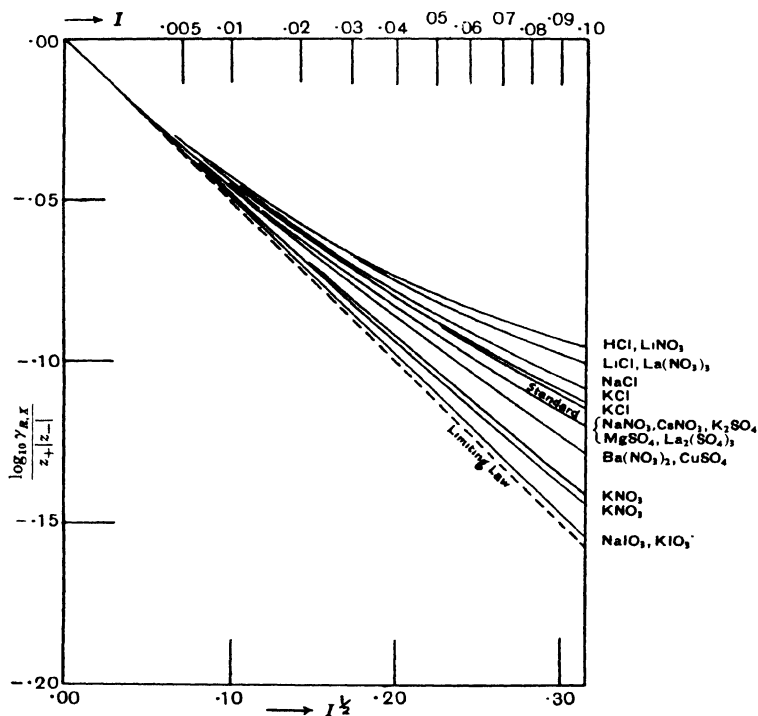



Fig. 3. Activity coefficients of various electrolytes calculated according to equation (17).

# CHAPTER X

## SURFACE LAYERS

**§ 1000. Introduction.** Surface phases constitute a state of matter to which statistical methods can be applied to construct the thermodynamic functions with much the same approximation as to liquid phases. A surface phase must strictly be regarded as all that volume of material surrounding an interface between two bulk phases in which the properties of the material differ appreciably from those of the bulk phases on either side. When the two bulk phases consist of the same pure substance the surface layer can differ only in structural arrangement; when the bulk phases contain more than one component the layer in general contains these components in changed proportions.

In the case of a surface layer or interface between two phases constructed of a single pure substance the main purpose of any theory must be to calculate the surface free energy. In the important case that the two phases are a liquid and its vapour this surface free energy per unit area is equal to the surface tension. In §§ 1016 *sqq.* we give a statistical theory of Macleod's equation for the surface tension of a liquid-vapour interface in terms of the difference in density of the liquid and the vapour. This theory is only very rough, and in general such surface phases are difficult to study theoretically, owing to the changes of structural arrangement involved.

The greater part of this chapter will be devoted to the consideration of films adsorbed on a liquid or a solid. The *a priori* calculation of the absolute value of the free energy for such a surface phase would be even more intractable than that of a volume phase of a single component, but its dependence on the amount of the substance or substances adsorbed is a much simpler problem, and it is with this problem that we shall be mainly concerned. In discussing such adsorbed films the underlying liquid or solid is regarded as providing a definite field of force for the adsorbed molecules. We shall confine our discussion to adsorbed layers at most one molecule thick, attached to the surface of a solid or of a liquid in which the molecules are practically insoluble. Such a layer may be conveniently referred to as a *monolayer*.

**§ 1001. Two types of monolayers.** We have to consider separately two distinct types of monolayer, which we shall refer to as *mobile monolayers* and *localized monolayers*. According to the model of a mobile monolayer some point in the adsorbed molecule (for example its centre of mass) is

bound tightly to the surface in the normal direction, with complete freedom of movement in the two directions in the surface, at a uniform potential except in so far as it interacts with other adsorbed molecules. This model is applicable to monolayers on liquids and perhaps also to monolayers on solids at high temperatures. But the more useful model for monolayers on solids is that of the localized monolayer, which is due to Langmuir. According to this model there are definite points of attachment on the solid surface, capable of accommodating just one adsorbed molecule. We shall refer to these points on the surface as sites. It should not be impossible to find a satisfactory mathematical technique for tracing the gradual transition from the localized monolayer to the mobile monolayer as the temperature is increased, but little work as yet has been done on this problem, and we shall not attempt to discuss it here.

§ **1002. Surface tension and spreading pressure.** Before proceeding to the statistical treatment of surfaces, we shall briefly note the thermodynamic relations for a surface phase, as these are not infrequently given wrongly. We associate with the interface a geometrical surface so placed that the total amount of a chosen component, say 1, which we shall call the reference component, is the same as if both bulk phases remained homogeneous right up to the geometrical surface. We then denote by $\Gamma_2^{(1)}, \Gamma_3^{(1)}, \ldots$ the excess amount per unit area of components $2, 3, \ldots$ over the amount there would have been if both bulk phases had remained homogeneous right up to the chosen surface. We also define the free energy $F^S$ of the surface by

$$F = F' + F'' + F^S, \tag{1002, 1}$$

where $F$ is the free energy of the assembly consisting of two bulk phases and the interface between them, and $F'$, $F''$ are the free energies of the two bulk phases calculated on the supposition that both these phases remain homogeneous right up to the chosen surface. The surface total energy $E^S$ and the surface entropy $S^S$ are defined analogously. The surface free energy $F^S$, thus defined, is related to the temperature, surface area $A$ and surface composition by

$$dF^S = -S^S dT + \gamma dA + \mu_2 d(\Gamma_2^{(1)}A) + \mu_3 d(\Gamma_3^{(1)}A) + \ldots; \tag{1002, 2}$$

$\gamma$ is called the surface tension. From (2) one can deduce the two further relations*

$$F^S = \gamma A + \mu_2 \Gamma_2^{(1)} A + \mu_3 \Gamma_3^{(1)} A + \ldots, \tag{1002, 3}$$

$$A\, d\gamma = -S^S dT - \Gamma_2^{(1)} A\, d\mu_2 - \Gamma_3^{(1)} A\, d\mu_3 - \ldots. \tag{1002, 4}$$

Formula (4) is the analogue for a surface phase of the Gibbs-Duhem relation

* See *M.T.* Chapter XII.

(601, 6). At constant temperature we can rewrite (4) in the more familiar form

$$-d\gamma = \Gamma_2^{(1)} d\mu_2 + \Gamma_3^{(1)} d\mu_3 + \ldots, \quad (T \text{ constant}) \qquad (1002, 5)$$

known as Gibbs' adsorption formula.

In the particular case of only a single component 1, formula (3) reduces to

$$F^S = \gamma A. \qquad (1002, 6)$$

In this case, but in this case only, the surface tension is equal to the surface free energy per unit area.

We have already mentioned that we shall be mainly concerned with surface films on an underlying solid or liquid phase, in which the substances forming the film are effectively insoluble. If we denote by $F^{\text{ads}}$ the contribution to $F^S$ of the adsorbed molecules forming the film, then $F^{\text{ads}}$ is determined by the number of these molecules of each type, by the temperature and by the area of the film. Let us now consider a surface of which one part of area $A$ is covered by the film and the remaining part is clean. Now suppose that the covered area $A$ increases by $dA$ and the clean area decreases by $dA$. Then the decrease of free energy will be

$$-dF^{\text{ads}} = -dF^S = -\gamma dA + \gamma_0 dA = (\gamma_0 - \gamma) dA \quad (T \text{ constant}), \; (1002, 7)$$

where $\gamma$ denotes the surface tension of the covered surface and $\gamma_0$ that of the clean surface. We may therefore regard $\gamma_0 - \gamma$ as the two-dimensional pressure that one would have to apply to the film to stop it from spreading. The quantity $\gamma_0 - \gamma$ is accordingly called the *spreading pressure*, and will be denoted by $\phi$. The relation $\phi = -\partial F^{\text{ads}}/\partial A$, which follows from (7), is the two-dimensional analogue of $P = -\partial F/\partial V$. The spreading pressure is a useful conception in the treatment of monolayers, and can be measured directly when the underlying phase is liquid. When the underlying phase is solid the physical significance of the spreading pressure of the film is still clear, although that of the surface tension of a solid surface is less obvious. In the treatment of monolayers, if one chooses the underlying substance as the reference substance and denotes the adsorbed substances by $A, B, \ldots$ instead of by $(2, 3, \ldots)$, we have in place of (5)

$$d\phi = \Gamma_A d\mu_A + \Gamma_B d\mu_B + \ldots \quad (T \text{ constant}). \qquad (1002, 8)$$

**§ 1003. Mobile monolayers.** We shall not devote much space to mobile monolayers purely for the reason that their statistical treatment is the exact analogue of that of bulk phases. A mobile monolayer of a single substance may be gaseous, liquid or solid* according to the degree of interaction between the adsorbed molecules.

* For a detailed account of monolayers on liquids dealing both with the elementary theory and the experimental data, see Adam, *The Physics and Chemistry of Surfaces*, Ed. 2 (Oxford, 1938).

If the interaction between the adsorbed molecules is entirely negligible, we have a two-dimensional perfect gas. We have already referred briefly to such an assembly in § 604. The partition function $l(T)$ for translation in two dimensions in an area $A$ is

$$l(T) = \frac{2\pi m kT}{h^2} A, \qquad (1003, 1)$$

and so the complete partition function $a(T)$ of an adsorbed molecule is

$$a(T) = l(T)\, j(T) = \frac{2\pi m kT}{h^2} A\, j(T), \qquad (1003, 2)$$

where $j(T)$ is the partition function for the internal degrees of freedom of the adsorbed molecule including vibration normal to the surface. The contribution $F^{\text{ads}}$ of the adsorbed molecules, $N$ in number, to the free energy is therefore, as in § 225,

$$\begin{aligned} F^{\text{ads}} &= -NkT \log a(T) + NkT(\log N - 1) \\ &= NkT \log\left\{\frac{N}{A}\frac{h^2}{2\pi m kT}\frac{1}{j(T)}\right\} - NkT. \end{aligned} \qquad (1003, 3)$$

The spreading pressure $\phi$ is therefore

$$\phi = -\frac{\partial F^{\text{ads}}}{\partial A} = \frac{NkT}{A}. \qquad (1003, 4)$$

This is the equation of state of an ideal mobile monolayer, analogous to a perfect gas. Such a monolayer is difficult to realize in practice owing to the high dilution required in order that the mutual interaction of the adsorbed molecules may be negligible.

If the mutual interactions of the adsorbed molecules are not entirely negligible but the deviations from ideality due to them are small, we have the exact analogue of slightly imperfect gases discussed in Chapter VII. The method of treatment is exactly analogous and we need not give details.* The contribution $F^{\text{ads}}$ of the adsorbed molecules to the free energy is now given by

$$F^{\text{ads}} = NkT \log \frac{h^2}{2\pi m kT j(T)} - kT \log \Omega(T), \qquad (1003, 5)$$

where $\Omega(T)$, conveniently called the partition function for the mutual interaction of the adsorbed molecules, is the two-dimensional analogue of the $\Omega(T)$ of Chapters VII and VIII. For small deviations from ideality $\Omega(T)$ is given by

$$\log \Omega(T) = N \log \frac{A}{N} + N + \frac{1}{2}\frac{N^2}{A}\int_0^\infty (e^{-\epsilon(r)/kT} - 1)\, 2\pi r\, dr, \qquad (1003, 6)$$

were $\epsilon(r)$ denotes the mutual potential energy of two adsorbed molecules

* See Mitchell, *Trans. Fara. Soc.* **31**, 980 (1935).

at a distance $r$ apart. Formula (6) is the exact two-dimensional analogue of (703, 15) for a single type of molecule. From (5) and (6) we deduce for the spreading pressure

$$\phi = -\frac{\partial F^{\text{ads}}}{\partial A} = kT\frac{\partial \log \Omega(T)}{\partial A} = \frac{NkT}{A} - \frac{1}{2}\frac{N^2}{A^2}kT\int_0^\infty (e^{-\epsilon(r)/kT}-1)\,2\pi r\,dr, \qquad (1003, 7)$$

this formula being the two-dimensional analogue of (704, 4) for a single type of molecule.

Formula (5) is of general validity, but the approximation (6) for $\Omega(T)$ is valid only for small deviations from ideality, and formulae (6) and (7) must not be applied in the regions of the critical state or of (two-dimensional) liquefaction. In these regions one has to use some method of evaluating $\Omega(T)$ such as that of Mayer from §§ 722 *sqq.* modified for two dimensions, or that described in §§ 808 *sqq.* for the three-dimensional case. This latter method has been applied by Devonshire† to compressed monolayers. We shall not give details of the treatment, which is exactly analogous to that used by Devonshire and Lennard-Jones for the three-dimensional assembly. Using $\epsilon^*$, as defined by formula (808, 5), to denote the minimum value of the mutual potential energy of two molecules, and $z$ to denote the number of nearest neighbours of a given molecule, we saw that the critical temperature $T_c$ for a three-dimensional assembly was given according to (810, 1) by

$$kT_c = z|\epsilon^*|/9. \qquad (1003, 8)$$

Devonshire finds that the critical temperature for the two-dimensional monolayer is given approximately by the similar relation

$$kT_c = z|\epsilon^*|/8{\cdot}6. \qquad (1003, 9)$$

In the three-dimensional assembly $z$ was assumed to have the value 12, as for close-packing. The analogous assumption for the two-dimensional assembly is $z = 6$ corresponding to triangular packing. Hence the ratio of the critical temperature for an adsorbed monolayer to the critical temperature of the same substance in bulk should be as (6/8·6):(12/9) or as 1:1·9. There are no quantitative data with which to compare this. But measurements‡ of the adsorption of xenon on liquid mercury show no trace of critical phenomena at temperatures considerably below the ordinary critical temperature of xenon.

Devonshire's treatment can obviously be extended to give the spreading pressure of a two-phase monolayer, one phase being a two-dimensional liquid, the other a two-dimensional gas. Such a calculation is, however, of

† Devonshire, *Proc. Roy. Soc.* A, **163**, 132 (1937).
‡ Cassel and Neugebauer, *J. Phys. Chem.* **40**, 523 (1936).

no practical value at the moment. For, whereas the energy of interaction is known as a function of the distance only for monatomic molecules or very symmetrical molecules such as $H_2$, $N_2$, all experimental data for the spreading pressures of mobile films are for large organic molecules.

§ **1004. Ideal localized monolayers.** We pass on now to consider localized monolayers, and start with those with negligible interaction between the adsorbed molecules. Such localized monolayers, like the mobile monolayers with the same property, may conveniently be called ideal. We denote by $\chi$ the minimum energy required to evaporate an adsorbed molecule from its lowest energy state in the monolayer, and taking the latter state as energy zero we denote the partition function for the internal degrees of freedom of the molecule including vibrations relative to its mean position in a site by $j^S(T)$. We denote by $a(T)$ the partition function for these internal degrees of freedom of an adsorbed molecule referred to the usual energy zero of the lowest internal state of the gaseous molecule at infinite separation. Then $a(T)$ is given by

$$a(T) = e^{\chi/kT} j^S(T), \tag{1004, 1}$$

but for the most part we shall not need to use this factorization of $a(T)$.

We denote the number of sites on the surface by $N_S$, and the number occupied by molecules of types $A, B, \ldots$ by $N_A, N_B, \ldots$. The number of empty sites will then be $N_S - \Sigma_A N_A$. The complete partition function for this monolayer is thus

$$g(N_A, N_B, \ldots)\, [a_A(T)]^{N_A} [a_B(T)]^{N_B} \ldots, \tag{1004, 2}$$

where $g(N_A, N_B, \ldots)$ denotes the number of distinguishable ways of distributing the adsorbed molecules over the sites. Thus $g(N_A, N_B, \ldots)$ is the number of ways of dividing $N_S$ sites into groups of $N_A, N_B, \ldots$ and $N_S - \Sigma_A N_A$. Hence

$$g(N_A, N_B, \ldots) = \frac{N_S!}{N_A!\, N_B! \ldots (N_S - \Sigma_A N_A)!}. \tag{1004, 3}$$

Substituting from (3) into (2) we obtain for the partition function of the monolayer

$$\frac{N_S!}{N_A!\, N_B! \ldots (N_S - \Sigma_A N_A)!} [a_A(T)]^{N_A} [a_B(T)]^{N_B} \ldots. \tag{1004, 4}$$

For the free energy $F^{\text{ads}}$ of the adsorbed monolayer we have then

$$\begin{aligned} \frac{F^{\text{ads}}}{kT} &= -\log\left[\frac{N_S!}{N_A!\, N_B! \ldots (N_S - \Sigma_A N_A)!} [a_A(T)]^{N_A} [a_B(T)]^{N_B} \ldots\right] \\ &= -N_S \log N_S + \Sigma_A N_A \log N_A + (N_S - \Sigma_A N_A) \log(N_S - \Sigma_A N_A) \\ &\qquad - \Sigma_A N_A \log a_A(T). \end{aligned} \tag{1004, 5}$$

For the partial potential $\mu_A$ of the molecules $A$ we have

$$\frac{\mu_A}{kT} = \frac{1}{kT}\left(\frac{\partial F^{\text{ads}}}{\partial N_A}\right)_{T,N,N_B} = \log\frac{N_A}{N_S - \Sigma_A N_A} - \log a_A(T)$$

$$= \log\frac{\theta_A}{1-\Sigma_A\theta_A} - \log a_A(T), \tag{1004, 6}$$

where $\theta_A, \theta_B, \ldots$ denote the fractions of sites occupied by molecules of types $A, B, \ldots$. The absolute activity of the molecules $A$ is given by

$$\lambda_A = e^{\mu_A/kT} = \frac{1}{a_A(T)}\frac{\theta_A}{1-\Sigma_A\theta_A}. \tag{1004, 7}$$

In the vapour phase the absolute activity $\lambda_A$ is, as we saw in Chapter v, given by

$$\lambda_A = \frac{p_A}{kT}\frac{h^3}{(2\pi m_A kT)^{\frac{3}{2}}\, j_A(T)}, \tag{1004, 8}$$

where $p_A$ denotes the partial pressure and $j_A(T)$ the partition function for the internal degrees of freedom of the gaseous molecule $A$. By comparing (7) with (8) we obtain the condition for equilibrium between the monolayer and the vapour phase in the form

$$\frac{\theta_A}{1-\Sigma_A\theta_A} = \frac{p_A}{p_A^0}, \tag{1004, 9}$$

where $p_A^0$ is defined by

$$p_A^0 = \frac{kT}{a_A(T)}\frac{(2\pi m_A kT)^{\frac{3}{2}}\, j_A(T)}{h^3}. \tag{1004, 10}$$

For the simple case of only a single type of adsorbed molecule formula (10) reduces to

$$\frac{\theta}{1-\theta} = \frac{p}{p^0}. \tag{1004, 11}$$

We can transform (11) to

$$\theta = \frac{p}{p^0 + p}. \tag{1004, 12}$$

Formulae (11) and (12) were first derived by Langmuir and are known as Langmuir's* adsorption isotherm Current proofs of these formulae are usually based on explicit assumptions as to the mechanism of deposition and evaporation. We see here that no such assumptions are necessary. The isotherms (9), (11) or (12) must hold whatever the kinetics of the processes, provided only that the molecules are adsorbed on to definite sites and do not interact with one another.

The form of Langmuir's adsorption isotherm is familiar and we shall not consider it in detail. Its limiting forms are

$$\theta \sim p/p_0 \quad (p \ll p^0), \tag{1004, 13}$$

$$\theta \sim 1 \qquad (p \gg p^0). \tag{1004, 14}$$

* Langmuir, *J. Am. Chem. Soc.* **40**, 1361 (1918).

The transition from the one limiting case to the other is more readily achieved by varying the temperature and so $p_0$, than by varying $p$ at a given temperature. At a single temperature it is usually impracticable to realize more than a short section of the isotherm.

Langmuir's adsorption formula is strictly applicable to an idealized solid surface, uniform in all directions, chemically inert and impermeable to the adsorbed gases. In all actual cases there arise complications through one or other of these conditions not being fulfilled. It is generally accepted that Langmuir's formula forms a good basis for the discussion of the adsorption of gases on solids, but it is too simple to give quantitative agreement with experiment.* We shall therefore not discuss in any detail the experimental data. As one example of an experimental study designed to examine critically the degree of validity of Langmuir's formula, we may refer to Wilkins' measurements† of the adsorption of argon, nitrogen and oxygen on smooth platinum foil for a range of temperatures and pressures.

**§ 1005. Atomic adsorption of diatomic molecules.** It can happen that the molecules of the monolayer are not identical with those in the gas. The important case is hydrogen which exists as molecules $H_2$ in the gas, but generally as H in the monolayer. We then have in the monolayer by (1004, 7)

$$\lambda_{\mathrm{H}} = \frac{1}{a_{\mathrm{H}}(T)} \frac{\theta_{\mathrm{H}}}{1-\theta_{\mathrm{H}}-\Sigma'\theta_A}, \tag{1005, 1}$$

where $\Sigma'$ denotes summation over all types of molecules other than hydrogen. In the gas phase we have, according to (1004, 8),

$$\lambda_{\mathrm{H}_2} = \frac{p_{\mathrm{H}_2}}{kT} \frac{h^3}{(2\pi m_{\mathrm{H}_2} kT)^{\frac{3}{2}} j_{\mathrm{H}_2}(T)}. \tag{1005, 2}$$

The condition for equilibrium between monolayer and gas is

$$\lambda_{\mathrm{H}_2} = \lambda_{\mathrm{H}}^2. \tag{1005, 3}$$

Substituting from (1) and (2) into (3), we obtain

$$\frac{\theta_{\mathrm{H}}}{1-\theta_{\mathrm{H}}-\Sigma'\theta_A} = \left(\frac{p_{\mathrm{H}_2}}{p^0_{\mathrm{H}_2}}\right)^{\frac{1}{2}}, \tag{1005, 4}$$

where $p^0_{\mathrm{H}_2}$ is defined by

$$p^0_{\mathrm{H}_2} = \frac{kT}{\{a_{\mathrm{H}}(T)\}^2} \frac{(2\pi m_{\mathrm{H}_2} kT)^{\frac{3}{2}} j_{\mathrm{H}_2}(T)}{h^3}. \tag{1005, 5}$$

Similar formulae could readily be derived for any analogous example of a difference of molecular state in the adsorbed and gas phases.

* See Adam, *The Physics and Chemistry of Surfaces*, Ed. 2 (Oxford, 1938).
† Wilkins, *Proc. Roy. Soc.* A, **164**, 510 (1938).

**§ 1006. Regular localized monolayers.** Although the adsorption isotherms of Langmuir's type in some cases give a fairly good semi-quantitative representation of the real isotherms, they are probably never accurate, and in some cases they become useless owing to the ignoring of the interactions between the adsorbed molecules. We shall now consider the effect of such interactions. We shall assume that each site has the same number $z$ of nearest neighbours, and that the total energy of interaction can be expressed as the sum of contributions of pairs of nearest neighbours. For the sake of brevity we shall confine ourselves to the case of only one type of adsorbed molecule, although the extension of the formulae to several types is straightforward.

We can easily adapt the notation introduced in § 1004 for application to monolayers with interactions between the adsorbed molecules. We first consider a monolayer of so few molecules that the number of pairs of neighbours is negligible. We denote by $\chi_0$ the value of $\chi$ for a molecule in such a monolayer, that is to say for a molecule adsorbed on a site with all the neighbouring sites unoccupied, and we denote the corresponding value of $a(T)$ by $a^0(T)$. We now consider a monolayer with $N_S$ sites, of which $N_A$ are occupied and $N_S - N_A$ are empty. If the number of pairs of neighbouring molecules in a particular configuration of the monolayer is $N_{AA}$, we assume that we can express the interaction energy, that is the amount by which the energy exceeds the value it would have if there were no pairs of neighbours by $N_{AA} 2w/z$. The factor $2/z$ is included for convenience. We assume that $a^0(T)$ is effectively independent of $N_{AA}$. The complete partition function of the monolayer is then

$$\Sigma_{N_{AA}} g(N_A, N_{AA})\, e^{-N_{AA} 2w/zkT} [a^0(T)]^{N_A}, \qquad (1006,1)$$

where $g(N_A, N_{AA})$ denotes the number of distinguishable configurations with $N_{AA}$ pairs of closest neighbours among the $N_A$ adsorbed molecules. We now define a quantity $\overline{\overline{N_{AA}}}$ by the equation

$$\begin{aligned}\Sigma_{N_{AA}} g(N_A, N_{AA})\, e^{-N_{AA} 2w/zkT} &= e^{-\overline{\overline{N_{AA}}} 2w/zkT}\, \Sigma_{N_{AA}} g(N_A, N_{AA}) \\ &= e^{-\overline{\overline{N_{AA}}} 2w/zkT} \frac{N_S!}{N_A!(N_S - N_A)!}, \qquad (1006,2)\end{aligned}$$

since $\Sigma_{N_{AA}} g(N_A, N_{AA})$ is the total number of distinguishable configurations in a monolayer of $N_A$ adsorbed atoms. Then the free energy $F^{\text{ads}}$ of the monolayer is given by

$$\begin{aligned}F^{\text{ads}}/kT = &-N_S \log N_S + N_A \log N_A + (N_S - N_A) \log(N_S - N_A) \\ &- N_A \log a^0(T) + \overline{\overline{N_{AA}}}\, 2w/zkT. \qquad (1006,3)\end{aligned}$$

If we then denote by $F^{\text{int}}$ the value by which $F^{\text{ads}}$ exceeds the value for an

ideal monolayer in which the interactions are ignored, we see by comparison of (3) with (1004, 5) that

$$F^{\text{int}} = \overline{\overline{N_{AA}}}\,2w/z. \tag{1006, 4}$$

We denote by $\overline{N_{AA}}$ the equilibrium value of $N_{AA}$ given by

$$\Sigma_{N_{AA}} N_{AA}\, g(N_A, N_{AA})\, e^{-N_{AA}2w/zkT} = \overline{N_{AA}}\, \Sigma_{N_{AA}}\, g(N_A, N_{AA})\, e^{-N_{AA}2w/zkT}. \tag{1006, 5}$$

By differentiating (2) with respect to $T$ and comparing with (5), we can show that

$$\overline{N_{AA}} = -T^2 \frac{\partial(\overline{\overline{N_{AA}}}/T)}{\partial T}. \tag{1006, 6}$$

It follows that the contribution $E^{\text{int}}$ of the interaction energy to the total energy is

$$E^{\text{int}} = -T^2 \frac{\partial(F^{\text{int}}/T)}{\partial T} = \overline{N_{AA}}\frac{2w}{z}, \tag{1006, 7}$$

as is physically obvious. The construction of all the thermodynamic functions is thus reduced to the evaluation of $\overline{\overline{N_{AA}}}$, or alternatively $\overline{N_{AA}}$, since the two are related by (6).

**§ 1007. Crude approximation.** Before deriving more exact formulae for $\overline{\overline{N_{AA}}}$ and $\overline{N_{AA}}$ we shall give some simpler formulae, which cannot be accurate but are a useful rough approximation to the accurate formulae. These formulae are obtained from the assumption of a completely random distribution of the adsorbed molecules in the monolayer. This crude assumption is exactly analogous to that used in § 818 to obtain the crude formulae for regular solutions.

Let us denote by $N_{A0}$ the numbers of pairs of neighbouring sites of which the one is occupied and the other is empty, and by $N_{00}$ the number of pairs of neighbouring sites both empty. Then, by counting all the $N_A$ occupied sites as the ends of neighbouring pairs, we see that we must have the relations

$$2N_{AA} + N_{A0} = zN_A, \quad 2\overline{N_{AA}} + \overline{N_{A0}} = zN_A; \tag{1007, 1}$$

$$2N_{00} + N_{A0} = z(N_S - N_A), \quad 2\overline{N_{00}} + \overline{N_{A0}} = z(N_S - N_A). \tag{1007, 2}$$

The assumption of a completely random distribution of the adsorbed molecules can be expressed in the form

$$2\overline{N_{AA}}\,.\,2\overline{N_{00}} = (\overline{N_{A0}})^2. \tag{1007, 3}$$

Eliminating $\overline{N_{A0}}$ and $\overline{N_{00}}$ from (1), (2) and (3), we obtain

$$2\overline{N_{AA}}(zN_S - 2zN_A + 2\overline{N_{AA}}) = (zN_A - 2\overline{N_{AA}})^2, \tag{1007, 4}$$

which reduces to

$$\overline{N_{AA}} = \tfrac{1}{2}zN_A^2/N_S. \tag{1007, 5}$$

Equations (3) and (5) are exactly equivalent. It may be easier for some readers to derive (5) itself from the assumption of randomness directly. Each occupied site has $z$ neighbours, and with perfectly random arrangements each site has a probability $N_A/N_S$ of being occupied. Hence the average number of neighbours of any given $N_A$ is $zN_A/N_S$. There are $N_A$ occupied sites in all and counting $zN_A/N_S$ neighbours for each counts each pair twice. We thus obtain (5). We shall now deduce the consequences* of the assumption of random distribution, expressed by (5).

According to (1006, 6) we have

$$\overline{\overline{N_{AA}}} = \overline{N_{AA}} = \tfrac{1}{2}zN_A^2/N_S. \qquad (1007,6)$$

Substituting from (6) into (1006, 3), we obtain

$$\frac{F^{\text{ads}}}{kT} = -N_S \log N_S + N_A \log N_A + (N_S - N_A)\log(N_S - N_A) - N_A \log a^0(T) + \frac{N_A^2}{N_S}\frac{w}{kT}. \qquad (1007,7)$$

For the partial potential $\mu$ of the adsorbed species we derive

$$\frac{\mu}{kT} = \frac{1}{kT}\left(\frac{\partial F^{\text{ads}}}{\partial N_A}\right)_{T,N_S} = \log\frac{N_A}{N_S - N_A} - \log a^0(T) + \frac{N_A}{N}\frac{2w}{kT}$$
$$= \log\frac{\theta}{1-\theta} - \log a^0(T) + \frac{2\theta w}{kT}, \qquad (1007,8)$$

where $\theta$ is the fraction of the sites that are occupied. The absolute activity $\lambda$ is given by

$$\lambda = e^{\mu/kT} = \frac{\theta}{1-\theta}e^{2\theta w/kT}\frac{1}{a^0(T)}. \qquad (1007,9)$$

By comparing this with formula (1004, 8) for the absolute activity in the gas phase, we deduce

$$p = p^0\frac{\theta}{1-\theta}e^{2\theta w/kT}, \qquad (1007,10)$$

where $p^0$ is defined by

$$p^0 = \frac{kT}{a^0(T)}\frac{(2\pi mkT)^{\frac{3}{2}}j^G(T)}{h^3} = \frac{(2\pi m)^{\frac{3}{2}}(kT)^{\frac{5}{2}}j^G(T)}{h^3 j^S(T)}e^{-\chi_0/kT}. \qquad (1007,11)$$

We have used the superscripts $G$ for the gas phase and $S$ for the surface phase. Writing $p(\theta)$ to denote the value of $p$ for the specified value of $\theta$, we deduce from (10)

$$p(\theta)\,p(1-\theta) = \{p(\tfrac{1}{2})\}^2, \qquad (1007,12)$$

and similarly from (9) we deduce

$$\lambda(\theta)\,\lambda(1-\theta) = \{\lambda(\tfrac{1}{2})\}^2, \qquad (1007,13)$$

* Fowler, *Proc. Camb. Phil. Soc.* **32**, 144 (1936).

where $\lambda(\theta)$ denotes the value of $\lambda$ for a given value of $\theta$. From (12) and (13) we see that $y = \log\{p(\theta)/p(\frac{1}{2})\} = \log\{\lambda(\theta)/\lambda(\frac{1}{2})\}$ is an odd function of $\theta - \frac{1}{2}$. Examples of $y$ plotted against $\theta$ for several values of $2w/kT$ are shown in Fig. 1.

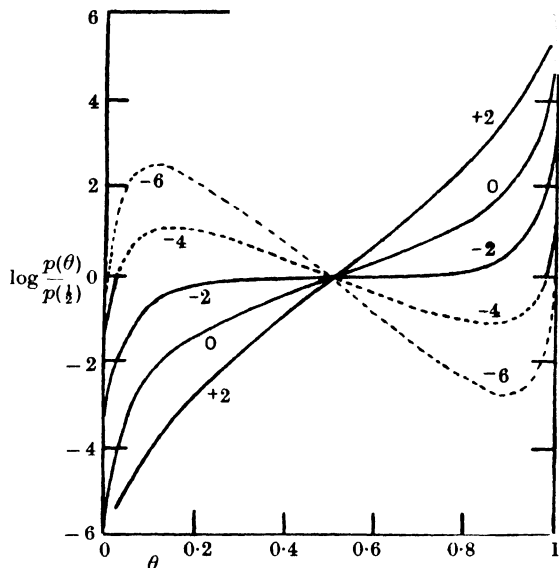



Fig. 1. Vapour pressures of regular monolayers (crude approximation). The figures attached to the curves are values of $w/kT$. The dotted portions of the curves represent unstable phases. The curve for $w/kT = 0$ is the ideal one and that for $w/kT = -2$ the critical one.

The curve for $w/kT = 0$ corresponds to an ideal localized monolayer and represents Langmuir's isotherm. The curves for $w/kT > 0$ and for $0 \geqslant w/kT > -2$ resemble Langmuir's isotherm in that $p$ or $\lambda$ increases steadily as $\theta$ increases from 0 to 1. The curves for $w/kT < -2$, however, have a central part where $p$ and $\lambda$ decrease as $\theta$ increases. This corresponds to an instability, and such a monolayer will split up into two stable monolayers. In the following section we shall consider in some detail the occurrence of two-phase monolayers.

We have in the present section tacitly assumed that the adsorbed molecules are identical with the molecules in the gas. When this is not the case, the formulae can easily be amended as described in § 1005. For example, if the gas consists of $H_2$ molecules which are adsorbed as H atoms, formula (9) for $\lambda$ remains unaltered provided $\lambda$ denotes $\lambda_H$. It is only the formula relating $\lambda$ to $p$ that has to be modified. Instead of formula (1004, 8) we have

to use as in § 1005

$$\lambda_{\mathrm{H}} = \{\lambda_{\mathrm{H}_2}\}^{\frac{1}{2}} = \left\{\frac{p_{\mathrm{H}_2}}{kT} \frac{h^3}{(2\pi m_{\mathrm{H}_2} kT)^{\frac{3}{2}} j_{\mathrm{H}_2}(T)}\right\}^{\frac{1}{2}}. \qquad (1007, 14)$$

The curves for $y$ are unaffected provided $y$ is now defined by

$$y = \log\{\lambda(\theta)/\lambda(\tfrac{1}{2})\} = \tfrac{1}{2}\log\{p(\theta)/p(\tfrac{1}{2})\}.$$

**§ 1008. Two-phase localized monolayers.** According to (1007, 9) we have

$$\frac{\partial y}{\partial \theta} = \frac{\partial \log \lambda}{\partial \theta} = \frac{1}{\theta} + \frac{1}{1-\theta} + \frac{2w}{kT}, \qquad (1008, 1)$$

$$\frac{\partial^2 y}{\partial \theta^2} = -\frac{1}{\theta^2} + \frac{1}{(1-\theta)^2}. \qquad (1008, 2)$$

From (2) we see that all the curves in Fig. 1 have a point of inflexion at $\theta = \frac{1}{2}$, and so the curves have their smallest slope at $\theta = \frac{1}{2}$. From (1) we see that this smallest slope is positive if $w/kT > -2$ and negative if $w/kT < -2$. When $w/kT = -2$ we have a horizontal point of inflexion. The temperature $T_c = -w/2k$ is therefore a critical one. At higher temperatures all values of $\theta$ are stable, while at lower temperatures values of $\theta$ in the neighbourhood of $\theta = \frac{1}{2}$ are unstable and phases with such values of $\theta$ will split into two stable phases.

We have now to determine the composition of the two stable phases into which an unstable phase splits. If we denote the two stable phases in mutual equilibrium by a single and a double prime, we must have

$$\lambda' = \lambda'', \qquad (1008, 3)$$

$$\phi' = \phi'', \qquad (1008, 4)$$

where $\phi$ denotes the spreading pressure. From (3) we see that the two phases are represented by points at the same height in Fig. 1. The condition (4) can be written as

$$\int_{\phi'}^{\phi''} d\phi = 0. \qquad (1008, 5)$$

But according to (1002, 8) we have

$$d\phi = \frac{N_S kT}{A} \theta \, d \log \lambda. \qquad (1008, 6)$$

Substituting from (6) into (5) we deduce

$$\int_{\lambda'}^{\lambda''} \theta \, d \log \lambda = 0. \qquad (1008, 7)$$

Formula (7) expresses the equality of the two areas formed by the curve corresponding to the single-phase isotherm and the horizontal line joining

the two phases in mutual equilibrium. But we have already noted that the curves are antisymmetrical about $\theta = \frac{1}{2}$ and so the two phases in mutual equilibrium must lie on the line $y = 0$. It follows that

$$\lambda' = \lambda'' = \lambda(\tfrac{1}{2}), \tag{1008, 8}$$

$$p' = p'' = p(\tfrac{1}{2}). \tag{1008, 9}$$

Substituting from (1007, 10) and (1007, 11) into (9), we obtain

$$p' = p'' = \frac{(2\pi m)^{\frac{3}{2}}(kT)^{\frac{5}{2}} j^G(T)}{h^3 j^S(T)} e^{-(\chi_0 - w)/kT}. \tag{1008, 10}$$

As a rough approximation we shall assume that the three translational degrees of freedom of an adsorbed molecule in the monolayer are effectively classical harmonic oscillations, and that all other internal degrees of freedom are the same in the adsorbed molecule as in the gaseous molecule. If we denote by $\nu$ the geometric mean of the frequencies for the three directions of vibration in the monolayer, the contribution of these vibrations to $j^S(T)$ is $(kT/h\nu)^3$. Substituting this value into (10) we obtain the approximation

$$p' = p'' = (2\pi m)^{\frac{3}{2}} \nu^3 (kT)^{-\frac{1}{2}} e^{-(\chi_0 - w)/kT}. \tag{1008, 11}$$

Differentiating (11) with respect to $T$ we obtain

$$kT^2 \frac{\partial \log p'}{\partial T} = \chi_0 - w - \tfrac{1}{2}kT. \tag{1008, 12}$$

According to (11) if one plots $\log(p'T^{\frac{1}{2}})$ against $1/T$ one should obtain a straight line of slope $-(\chi_0 - w)/k$. Since in the experimental range the variation of the factor $T^{-\frac{1}{2}}$ in (11) is not serious, one would also expect to obtain an effectively straight line by plotting $\log p' = \log p''$ against $1/T$; the slope of this straight line should be $-(\chi_0 - w - \frac{1}{2}kT)/k$.

As defined above $p'$ (or $p''$) is the vapour pressure of a two-phase monolayer, but at temperatures well below the critical temperature $T_c$ we can obtain and use an alternative definition. Consider for example the temperature $T = -w/4k$, just half the critical temperature. The two monolayers in equilibrium have according to (1007, 10) and (9) compositions given by the two roots other than $\theta = \frac{1}{2}$ of the equation

$$\frac{\theta}{1-\theta} = e^{-4(1-2\theta)}. \tag{1008, 13}$$

These roots are $\theta' = 0{\cdot}021$ and $\theta'' = 0{\cdot}979$. At lower temperatures $\theta'$ is still nearer to zero and $\theta''$ still nearer to unity. At each temperature well below $T_c$, if the pressure of the vapour is gradually increased, there is then a definite pressure $p'$ at which the equilibrium value of $\theta$ jumps from a value $\theta'$ not much different from zero to a value $\theta''$ not much different from unity.

Conversely for a given pressure $p$ there will be some temperature $T$ at which $p'(T) = p$. For a slightly higher temperature we have $p'(T) > p$, and so the equilibrium value of $\theta$ for the given $p$ will be less than $\theta'(T)$, differing but slightly from zero. For a slightly lower temperature on the other hand we have $p'(T) < p$ and so the equilibrium value of $\theta$ for the given $p$ will exceed $\theta''(T)$, differing but slightly from unity. Thus for a given $p$ as the temperature is lowered there will be a temperature at which the equilibrium value of $\theta$ jumps suddenly from a value near zero to a value near unity.

**§ 1009. Comparison with experiment.** There are no equilibrium measurements corresponding to the theory of two-phase localized monolayers, but an indirect comparison of the theory with certain kinetic experiments can be made. In these experiments a stream of metal vapour falls on a plate at a given temperature, the metal atoms making a given number of impacts on unit area in unit time. It is found that at temperatures greater than a certain temperature $T_d$, depending on the rate of bombardment, the metal is not deposited, but that at temperatures less than $T_d$ the metal is deposited in bulk. We may therefore call $T_d$ the temperature of deposition. What is observed has therefore nothing directly to do with the formation of an equilibrium monolayer to which the theory applies, but one can see that it can be related to the underlying equilibrium problem. The existence of a sharp deposition temperature $T_d$ has been discussed previously by Langmuir† and by Frenkel‡ from a more kinetic standpoint than that adopted here.

Under complete equilibrium conditions between a two-phase monolayer and the vapour phase, the vapour pressure $p'$ (or $p''$) is given approximately by (1008, 11). The number $n$ of molecules from the vapour phase striking unit area in unit time is according to (334, 2)

$$n = p'/(2\pi m kT)^{\frac{1}{2}}. \qquad (1009, 1)$$

Substituting from (1008, 11) into (1) we obtain

$$n = \frac{2\pi m\nu^3}{kT} e^{-(\chi_0 - w)/kT}. \qquad (1009, 2)$$

Let us denote by $n^*$ the number of molecules striking unit area in unit time under the non-equilibrium conditions of the experiments mentioned above. We assume that the probability that a molecule hitting the surface becomes adsorbed either is almost unity or at least is almost independent of its velocity. Then the surface will at the most become covered to an extent $\theta^*$ at which the rate of evaporation of adsorbed molecules from unit area in

† Langmuir, *Proc. Nat. Acad. Sci.* **3**, 141 (1917).
‡ Frenkel, *Zeit. Phys.* **26**, 117 (1924).

unit time is equal to $n^*$. For a given value of the temperature $T$ of the surface, $\theta^*$ will, as explained in the previous section, be only slightly greater than zero if $n^* < n$ and will be only slightly less than unity if $n^* > n$. If then we gradually lower the temperature $T$, the surface will not become covered appreciably until the temperature reaches the value $T_d$ at which $n = n^*$, when the surface will suddenly tend to be practically completely covered. Actually as soon as the temperature becomes lower than $T_d$, not only does the surface become covered with a monolayer but further layers of metal atoms deposit in bulk on top of the monolayer. This secondary occurrence need not however concern us. The deposition temperature $T_d$ for given $n^*$ is then according to (2) given by

$$n^* = \frac{2\pi m\nu^3}{kT_d} e^{-(\chi_0 - w)/kT_d}. \tag{1009, 3}$$

The temperature dependence of the non-exponential factor in (3) is unimportant compared with that of the exponential factor. If follows that if $\log n^*$ is plotted against $1/T_d$ one should obtain a practically straight line of slope $-(\chi_0 - w - kT_d)/k$, and the extrapolated value of $\log n^*$ for $1/T_d = 0$ should be $2\pi m\nu^3/kT_d$.

Accurate experiments which can be compared with the theory on this basis have been recorded by Cockcroft.† His results for the condensation of cadmium on copper are shown in Fig. 2 in which $\log_{10} n^*$ is plotted against $1/T_d$. The observed relation approximates closely to

$$\log_{10} n^* = 22{\cdot}75 - 1250/T_d. \tag{1009, 4}$$

Comparing this empirical relation with (3), we deduce that

$$(\chi_0 - w - kT_d)/k = 2{\cdot}303 \times 1250 = 2880\,\text{deg.}$$

In the middle of the experimental temperature range $1/T_d = 0{\cdot}007\,\text{deg.}^{-1}$ and so $(\chi_0 - w - kT_d)/kT_d \simeq 0{\cdot}007 \times 2880 \simeq 20$. The available data do not enable us to estimate $\chi_0$ and $w$ separately. The theory, however, requires that $T_d \ll T_c = -w/2k$ or $-w/kT_d \gg 2$, which is consistent with the data.

We can also estimate $\nu$ the average frequency of vibration of an adsorbed atom by comparing the empirical relation (4) with the theoretical formula (3). We thus find

$$\nu^3 = 10^{22{\cdot}75} kT_d/2\pi m \simeq 10^{30}\,\text{sec.}^{-3},$$

so that $\nu \simeq 10^{10}\,\text{sec.}^{-1}$. The corresponding characteristic temperature defined by $\Theta = h\nu/k$ is approximately $\frac{1}{2}$ deg. This low value is inconsistent with the assumed model of a localized monolayer. If an adsorbed atom were so loosely

* Cockcroft, *Proc. Roy. Soc.* A, **119**, 293 (1928).

bound to the surface, as such a low frequency implies, the monolayer would become a mobile one. The theory is therefore inadequate to explain the experimental data quantitatively.

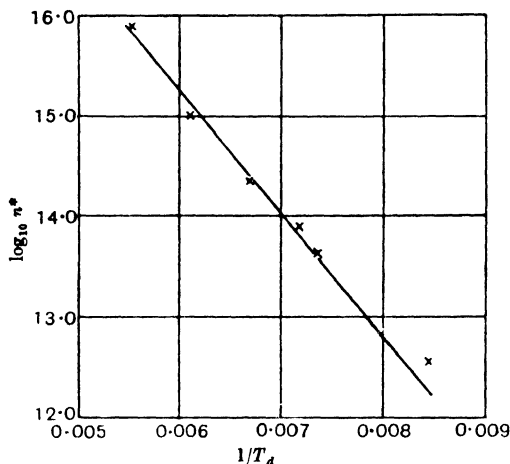



Fig. 2. Dependence of deposition temperature $T_d$ on $n^*$ the number of impacts per cm.² per sec.

**§ 1010. Refined treatment of localized monolayers.** All the results which we have obtained for localized monolayers with interactions between the adsorbed molecules have been based on the assumption of an energy formula which can only be expected to hold for a random distribution of the adsorbed molecules among the surface sites. We have already mentioned that this assumption leads to useful rough approximations, but it cannot be accurate, since evidently each configuration of low energy will occur more frequently than one of higher energy. We may expect, as in the analogous discussion of regular solutions in Chapter VIII, to obtain more accurate results by replacing the equation (1007, 4) by

$$2\overline{N_{AA}}(zN_S - 2zN_A + 2\overline{N_{AA}}) = (zN_A - 2\overline{N_{AA}})^2 e^{-2w/zkT}. \quad (1010, 1)$$

This formula is of the type of a quasi-chemical equilibrium, the extra factor $e^{-2w/zkT}$ corresponding to the increase of energy $2w/z$ when a new pair of neighbours is formed among the adsorbed atoms. We postpone a detailed proof of equation (1) to the next section. We shall meanwhile assume (1) to be correct, and use it to investigate the degree of inaccuracy of the results obtained on the assumption of random distribution of configurations. It is convenient to define the dimensionless quantity $x$ by

$$x = N_{AA}/\tfrac{1}{2}zN_S. \quad (1010, 2)$$

We can then rewrite (1) as

$$\bar{x}(1-2\theta+\bar{x}) = (\theta-\bar{x})^2 e^{-2w/zkT}, \tag{1010, 3}$$

in which $\theta$ denotes the fraction $N_A/N_S$ of sites occupied. Equation (3) is a quadratic in $\bar{x}$ with the solution

$$\bar{x} = \theta + \frac{\{1-4\theta(1-\theta)(1-e^{-2w/zkT})\}^{\frac{1}{2}}-1}{2(1-e^{-2w/zkT})}$$

$$= \theta - \frac{2\theta(1-\theta)}{\{1-4\theta(1-\theta)(1-e^{-2w/zkT})\}^{\frac{1}{2}}+1}. \tag{1010, 4}$$

This formula takes the place of the crude approximation

$$\bar{x} = \theta^2 = \theta - \theta(1-\theta), \tag{1010, 5}$$

corresponding to formula (1007, 5) of the crude treatment.

Let us now compare the refined formula (4) with the crude formula (5). The discrepancy is greatest for $\theta = \frac{1}{2}$ for which (4) becomes

$$\bar{x} = \tfrac{1}{2}(1+e^{w/zkT})^{-1}. \tag{1010, 6}$$

For attractions between the adsorbed molecules ($w<0$) and for $T = -w/2k$, that is for the temperature which is critical according to the crude treatment, (6) becomes

$$\bar{x} = \tfrac{1}{2}(1+e^{-2/z})^{-1}. \tag{1010, 7}$$

For $z = 6$ this gives $\bar{x} = 0{\cdot}291$ as compared with $\bar{x} = 0{\cdot}250$ given by (5). At lower temperatures the error in $\bar{x}$ for $\theta = \frac{1}{2}$ would be greater, but such values of $\theta$ become unstable. For stable values of $\theta$ the error in $\bar{x}$ due to using (5) instead of (4) never exceeds 20 % for attractions ($w<0$) between the adsorbed molecules. We thus see that the crude approximation is by no means accurate, but in some cases the inaccuracy will be small enough for the approximation to be useful.

The greater inaccuracy of the crude approximation for monolayers as compared with the analogous approximation for regular solutions is entirely due to the smaller value of $z$, which is only 6 for a close-packed two-dimensional lattice but 12 for a close-packed three-dimensional lattice. We may note that if we make $z \to \infty$ keeping $w$ constant, formula (4) reduces to (5) and the difference between the crude and the refined formulae disappears; but values of $z$ greater than those mentioned above have no obvious physical importance.

**§ 1011. Grand partition function for localized monolayers.** In the previous section we assumed the quasi-chemical equilibrium condition (1010, 1), and this still awaits proof. We can conveniently derive this condition, and in fact all the equilibrium properties of localized monolayers, by the use of the grand partition function. We therefore proceed to construct

this and use it. Before, however, applying it to monolayers with interactions between the adsorbed molecules we shall apply it to ideal monolayers, and verify the relations already obtained for these. For the sake of brevity we confine ourselves to a single type $A$ of adsorbed molecules.

We recall that the ordinary partition function for a surface with $N_S$ sites of which $N_A$ are occupied is given by (1006, 1). The corresponding formula for the grand partition function, when the absolute activity of the adsorbed molecules is $\lambda$, is

$$\Xi = \Sigma_{N_A} \Sigma_{N_{AA}} g(N_A, N_{AA})\, e^{-N_{AA}2w/zkT}\{a^0(T)\}^{N_A} \lambda^{N_A}. \qquad (1011, 1)$$

The coefficients $g(N_A, N_{AA})$ are not easily evaluated, but they must satisfy the relation

$$\Sigma_{N_{AA}} g(N_A, N_{AA}) = \frac{N_S!}{N_A!(N_S - N_A)!}. \qquad (1011, 2)$$

Owing to this relation the formula for $\Xi$ simplifies considerably for the special case of an ideal monolayer.

For an ideal monolayer $w$ vanishes by definition, and (1) reduces to

$$\Xi = \Sigma_{N_A} \frac{N_S!}{N_A!(N_S - N_A)!}\{\lambda a^0(T)\}^{N_A} = \{1 + \lambda a^0(T)\}^{N_S}. \quad (1011, 3)$$

The equilibrium (average) value of $N_A$ is then given by

$$\overline{N_A} = \lambda \frac{\partial \log \Xi}{\partial \lambda} = N_S \frac{\lambda a^0(T)}{1 + \lambda a^0(T)}, \qquad (1011, 4)$$

and so the equilibrium value for the fraction of sites occupied is

$$\theta = \frac{\overline{N_A}}{N_S} = \frac{\lambda a^0(T)}{1 + \lambda a^0(T)}. \qquad (1011, 5)$$

This can be transformed to

$$\frac{\theta}{1 - \theta} = \lambda a^0(T), \qquad (1011, 6)$$

in agreement with (1004, 7).

We now return to regular monolayers for which $w$ is not zero. The grand partition function is given by (1), but it can be shown that we may with negligible error replace $\Xi$ by its largest term, $\Xi_{(N^*)}$ say, given by

$$\Xi_{(N^*)} = g(N_A^*, N_{AA}^*)\, e^{-N_{AA}^* 2w/zkT}\{\lambda a^0(T)\}^{N_A^*}. \qquad (1011, 7)$$

The average (equilibrium) values of $N_A$, $N_{AA}$ are then given by

$$\overline{N_A} = N_A^*, \qquad (1011, 8)$$

$$\overline{N_{AA}} = N_{AA}^*. \qquad (1011, 9)$$

We have already mentioned that the coefficients $g(N_A, N_{AA})$ are not expressible in a simple form, and so we cannot evaluate either $\Xi$ or $\Xi_{(N^*)}$ by any

direct method. We therefore use the device described in §§ 608–610,† which for the reader's convenience we set out again at length adapted to the notation of the present problem. For brevity we introduce the symbols $\xi_A$ and $\eta_{AA}$ defined by

$$\xi_A = \lambda a^0(T), \quad (1011,10)$$

$$\eta_{AA} = e^{-2w/zkT}, \quad (1011,11)$$

so that (1011, 7) becomes

$$\Xi_{(N^*)} = g(N^*_A, N^*_{AA})\,\eta_{AA}^{N^*_{AA}}\,\xi_A^{N^*_A}. \quad (1011,12)$$

We further define $\xi$, $\eta$, $\gamma$ by

$$\xi^{N_S} = \xi_A^{N^*_A}, \quad (1011,13)$$

$$\eta^{\frac{1}{2}zN_S} = \eta_{AA}^{N^*_{AA}}, \quad (1011,14)$$

$$\gamma^{N_S} = g(N^*_A, N^*_{AA}). \quad (1011,15)$$

Thus $\xi$ is the geometrical mean contribution of each site, empty or occupied, to the factor $\xi_A^{N^*_A}$ in $\Xi_{(N^*)}$; $\eta$ is the geometrical mean contribution of each pair of neighbouring sites to the factor $\eta_{AA}^{N^*_{AA}}$ in $\Xi_{(N^*)}$; $\gamma$ is the geometrical mean contribution of each site to the factor $g(N^*_A, N^*_{AA})$ in $\Xi_{(N^*)}$. We can then write

$$\Xi_{(N^*)} = \gamma^{N_S}\xi^{N_S}\eta^{\frac{1}{2}zN_S}. \quad (1011,16)$$

Finally we denote by $\eta_A$ the geometrical mean contribution of a pair of neighbouring sites, of which the first is occupied by a molecule $A$, to the factor $\eta_{AA}^{N^*_A}$ in $\Xi_{(N^*)}$. From these definitions we can write down various alternative expressions equal in magnitude to $\Xi$, in particular the two following

$$\Xi_1 = (1+\xi_A\eta_A^z)\,\gamma^{N_S-1}\xi^{N_S-1}\eta^{\frac{1}{2}zN_S-z}, \quad (1011,17)$$

$$\Xi_2 = \{1+2\xi_A\eta_A^{z-1}+(\xi_A\eta_A^{z-1})^2\eta_{AA}\}\,\gamma^{N_S-2}\xi^{N_S-2}\eta^{\frac{1}{2}zN_S-2z+1}. \quad (1011,18)$$

It is naturally only an approximation to assume that $\Xi$ can be expressed in either of these forms. The form $\Xi_1$ corresponds to regarding the assembly as a single site in a field due to the occupants of the remaining $N-1$ sites, while the form $\Xi_2$ corresponds to regarding the assembly as a pair of neighbouring sites in a field due to the occupants of the remaining $N-2$ sites. In the first factor in (17) the term unity is the contribution of the unoccupied site, and the term $\xi_A\eta_A^z$ is the contribution of the occupied site. Hence the frequency of occupation of the given site, which is equal to the average fraction $\theta$ of all sites occupied, is given by

$$\theta = \xi_A\eta_A^z/(1+\xi_A\eta_A^z). \quad (1011,19)$$

We may argue more formally and say that $\theta$ is the average number of occu-

† The treatment given here is a variant of that of Peierls, *Proc. Camb. Phil. Soc.* **32**, 471 (1936).

pants of the chosen site, and therefore $\theta = \xi_A\, \partial/\partial\xi_A(\log \Xi_1)$. This leads equally to (19). In the first factor in (18) the term unity is the contribution of the pair of empty sites; a term $\xi_A \eta_A^{z-1}$ is the contribution when the first site is full and the second empty; there is an equal contribution when the first site is empty and the second is full; the term $(\xi_A \eta_A^{z-1})^z \eta_{AA}$ is the contribution of the pair of full sites. Hence the frequency of occupation of one of the sites, which is equal to the average fraction $\theta_A$ of all sites occupied, is given by

$$\theta = \frac{\xi_A \eta_A^{z-1} + (\xi_A \eta_A^{z-1})^2 \eta_{AA}}{1 + 2\xi_A \eta_A^{z-1} + (\xi_A \eta_A^{z-1})^2 \eta_{AA}}. \tag{1011, 20}$$

Using the notation introduced at the beginning of § 1007, we see further from the first factor of (18) that

$$\overline{N_{00}} : \overline{N_{A0}} : \overline{N_{AA}} = 1 : 2\xi_A \eta_A^{z-1} : (\xi_A \eta_A^{z-1})^2 \eta_{AA}, \tag{1011, 21}$$

from which it follows that

$$4\overline{N_{00}}\,\overline{N_{AA}}/\overline{N_{A0}}^2 = \eta_{AA} = e^{-2w/zkT}, \tag{1011, 22}$$

and this is precisely equivalent to (1010, 1), the equation of quasi-chemical equilibrium.

**§ 1012. Refined formulae for adsorption equilibrium.** According to formulae (1010, 2) and (1010, 4) we can write for $\overline{N_{AA}}$

$$\overline{N_{AA}} = zN_S \left\{ \tfrac{1}{2}\theta - \frac{\theta(1-\theta)}{\beta+1} \right\}, \tag{1012, 1}$$

where for brevity we have introduced a quantity $\beta$ defined by

$$\beta = \{1 - 4\theta(1-\theta)(1 - e^{-2w/zkT})\}^{\frac{1}{2}}. \tag{1012, 2}$$

According to (1006, 7) the contribution of the interaction energy to the total energy is

$$E^{\text{int}} = N_S w \left\{ \theta - \frac{2\theta(1-\theta)}{\beta+1} \right\}. \tag{1012, 3}$$

The corresponding contribution to the free energy is derived from (3) by using (1006, 4) and (1006, 6). The algebra is exactly analogous to that in § 819 and we need not give the steps. We eventually find

$$\begin{aligned} F^{\text{int}} &= N_S w \left\{ \theta + \frac{\frac{1}{2}zkT}{w} \left[ \theta \log \frac{\beta - 1 + 2\theta}{2\theta} + (1-\theta) \log \frac{\beta + 1 - 2\theta}{2(1-\theta)} - \log \frac{\beta+1}{2} \right] \right\} \\ &= N_S w \left\{ \theta + \frac{\frac{1}{2}zkT}{w} \left[ \theta \log \frac{(\beta - 1 + 2\theta)(1-\theta)}{(\beta + 1 - 2\theta)\theta} + \log \frac{\beta + 1 - 2\theta}{(\beta+1)(1-\theta)} \right] \right\}. \end{aligned} \tag{1012, 4}$$

Consequently for the free energy $F^{\text{ads}}$ of the monolayer we have instead of the crude approximation (1007, 7) the more accurate formula

$$\frac{F^{\text{ads}}}{N_S kT} = \theta \log \frac{\theta}{1-\theta} + \log(1-\theta) - \theta \log a^0(T) + \theta \frac{w}{kT}$$
$$+ \tfrac{1}{2}z\left\{\theta \log \frac{(\beta-1+2\theta)(1-\theta)}{(\beta+1-2\theta)\theta} + \log \frac{\beta+1-2\theta}{(\beta+1)(1-\theta)}\right\}. \quad (1012, 5)$$

For the absolute activity $\lambda$ and the partial potential $\mu$ of the adsorbed molecules we derive, after rather long but straightforward algebra,

$$\log \lambda = \frac{\mu}{kT} = \frac{1}{kT}\left(\frac{\partial F^{\text{ads}}}{\partial N_A}\right)_{T,N_S}$$
$$= \log \frac{\theta}{1-\theta} - \log a^0(T) + \frac{w}{kT} + \tfrac{1}{2}z \log \frac{(\beta-1+2\theta)(1-\theta)}{(\beta+1-2\theta)\theta}, \quad (1012, 6)$$

all other terms cancelling. A formula equivalent to (6) was first obtained by Lacher.* If we substitute for $\beta$ its value given by (2), expand in powers of $w/zkT$ and neglect higher powers than the first, formula (5) reduces to the crude formula (1007, 7) and formula (6) reduces similarly to (1007, 8).

For the equilibrium vapour pressure $p(\theta)$ over a monolayer, with a fraction $\theta$ of the sites occupied, we deduce, using (1004, 8) for $\lambda$ in the gas phase

$$p(\theta) = p^0 \frac{\theta}{1-\theta} e^{w/kT} \left\{\frac{(\beta-1+2\theta)(1-\theta)}{(\beta+1-2\theta)\theta}\right\}^{\frac{1}{2}z}. \quad (1012, 7)$$

By using formula (2) we can rewrite (7) in the alternative forms

$$p(\theta) = p^0 \frac{\theta}{1-\theta} e^{2w/kT} \left(\frac{\beta-1+2\theta}{2\theta}\right)^z, \quad (1012, 8)$$

$$p(\theta) = p^0 \frac{\theta}{1-\theta} \left(\frac{2-2\theta}{\beta+1-2\theta}\right)^z. \quad (1012, 9)$$

In particular for $\theta = \frac{1}{2}$ we have

$$\beta_{\theta=\frac{1}{2}} = e^{-w/zkT}, \quad p(\tfrac{1}{2}) = p^0 e^{w/kT}. \quad (1012, 10)$$

One can verify from any of the formulae (7), (8) or (9) that

$$p(\theta) \times p(1-\theta) = \{p(\tfrac{1}{2})\}^2. \quad (1012, 11)$$

Hence $y = \log\{p(\theta)/p(\frac{1}{2})\} = \log\{\lambda(\theta)/\lambda(\frac{1}{2})\}$ is an odd function of $\theta - \frac{1}{2}$. The corresponding curves therefore have a point of inflexion at $(\theta = \frac{1}{2}, y = 0)$ and thus resemble those in Fig. 1 given by the crude formula of § 1007. The curves have their greatest slope at the point of inflexion $(\theta = \frac{1}{2}, y = 0)$. If this slope is negative the middle part of the curve represents unstable phases, and such a phase will split into two stable phases. By the same reasoning as in

* Lacher, *Proc. Camb. Phil. Soc.* **33**, 518 (1937).

§ 1008 we can show that values of $\theta$ for the two stable phases in equilibrium with each other are the two roots of the equation $y = 0$ other than $\theta = \frac{1}{2}$ and are equally distant from $\theta = \frac{1}{2}$. The critical temperature $T_c$, which is the maximum temperature at which splitting into two phases occurs, is determined by the condition that $dy/d\theta = 0$ for $\theta = \frac{1}{2}$, or alternatively $\partial p(\theta)/\partial\theta = 0$ for $\theta = \frac{1}{2}$. Applying this condition to (9) we find

$$e^{-w/zkT_c} = z/(z-2), \tag{1012, 12}$$

or

$$\frac{-w}{kT_c} = z \log \frac{z}{z-2}. \tag{1012, 13}$$

If we assume $z = 6$ corresponding to two-dimensional closest packing, this gives $-w/kT_c = 6 \log \frac{6}{4} = 2{\cdot}43$, whereas the crude treatment of § 1008 led to $-w/kT_c = 2$, which agrees formally with (13) in the limit as $z \to \infty$. We have already noted that for a given value of $w$ the crude solution corresponds formally to the refined solution in the limit $z \to \infty$.

To sum up we see that the refined treatment leads to results differing quantitatively from the crude treatment, but to nothing qualitatively new. There are no available experimental data of sufficient accuracy and completeness to test the theory quantitatively and we shall not use it.

We can use formula (5) for $F^{\text{ads}}$ to calculate the spreading pressure. We have by definition

$$\phi A = -A\left(\frac{\partial F^{\text{ads}}}{\partial A}\right)_{T,N_A} = -N_S\left(\frac{\partial F^{\text{ads}}}{\partial N_S}\right)_{T,N_A}. \tag{1012, 14}$$

Substituting from (5) into (14) we obtain after long but straightforward algebra

$$\frac{\phi A}{N_S kT} = \log \frac{1}{1-\theta} - \tfrac{1}{2}z \log \frac{\beta+1-2\theta}{(\beta+1)(1-\theta)}, \tag{1012, 15}$$

all other terms cancelling. By comparing (5) with (6) and (15) we can verify the thermodynamically necessary equality

$$F^{\text{ads}} + \phi A = N_A \mu. \tag{1012, 16}$$

**§ 1013. Spreading pressure of ideal monolayers.** The spreading pressure $\phi$ of an adsorbed film of area $A$ is related to the grand partition function by

$$\phi = \frac{kT}{A} \log \Xi. \tag{1013, 1}$$

For an ideal localized monolayer according to (1011, 3) this becomes

$$\phi = \frac{N_S}{A} kT \log\{1 + \lambda a^0(T)\}. \tag{1013, 2}$$

According to (1011, 5) we have

$$1-\theta = \{1 + \lambda a^0(T)\}^{-1}, \tag{1013, 3}$$

and substituting this into (2) we obtain

$$\phi = \frac{N_S}{A} kT \log\left(\frac{1}{1-\theta}\right), \tag{1013, 4}$$

agreeing with formula (1012, 15) when $w = 0$, so that $\beta = 1$. This formula for the spreading pressure of an ideal *localized* monolayer is not to be confused with that for the spreading pressure of an ideal *mobile* monolayer, which can be written according to (1003, 4)

$$\phi = \frac{N_A}{A} kT. \tag{1013, 5}$$

From (4) and (5) we see that for a given number of adsorbed molecules per unit area the spreading pressure is directly proportional to the temperature for both kinds of ideal monolayers, localized and mobile. It has sometimes been inferred incorrectly that this proportionality implies that the monolayer is mobile. Actually the proportionality follows simply from the absence of mutual interaction between adsorbed molecules.

§ **1014. Gibbs' adsorption formula.** It is of interest to verify that Gibbs' adsorption formula in the form (1002, 8), usually obtained thermodynamically, can be derived directly from the properties of the grand partition function. We need not restrict ourselves to a single type of adsorbed molecule, and we denote the several types by $A, B, \ldots$. Then the equilibrium number of adsorbed molecules of each type is given by relations of the form

$$N_A = \lambda_A \frac{\partial \log \Xi}{\partial \lambda_A}, \tag{1014, 1}$$

while the spreading pressure $\phi$ is related to $\Xi$ by

$$\phi A = kT \log \Xi. \tag{1014, 2}$$

By eliminating $\Xi$ from (1) and (2) we obtain

$$\Gamma_A = \frac{N_A}{A} = \frac{\lambda_A}{A} \frac{\partial}{\partial \lambda_A}\left(\frac{\phi A}{kT}\right) = \frac{1}{kT} \frac{\partial \phi}{\partial \log \lambda_A} = \frac{\partial \phi}{\partial \mu_A}, \tag{1014, 3}$$

which is equivalent to (1002, 8).

§ **1015. Energy of desorption.** Having obtained formulae for the free energy of monolayers of various types, we can always derive formulae for the corresponding total energy by means of the relation

$$E^{\text{ads}} = -T^2 \frac{\partial (F^{\text{ads}}/T)}{\partial T}. \tag{1015, 1}$$

We can insert into (1) any of the formulae obtained for $F^{\text{ads}}$. The resulting

formulae for $E^{ads}$ will all contain a term such as $N_A kT^2 \, \partial \log a^0(T)/\partial T$, which we cannot evaluate accurately. To obtain results of interest we are compelled to use some kind of approximation. The simplest approximate assumption is that already used in § 1009, that the three translational degrees of freedom of an adsorbed molecule in a localized monolayer behave as classical harmonic oscillations and that the internal degrees of freedom are the same as in the gas phase. When we use these simple approximations, we obtain for the energy of desorption of $N_A$ molecules from an ideal localized monolayer

$$N_A(\chi - \tfrac{3}{2}kT). \tag{1015, 2}$$

Similarly for a monolayer with interaction between the adsorbed molecules we obtain an energy of desorption for the whole layer

$$N_A(\chi_0 - \tfrac{3}{2}kT) - \overline{N_{AA}}\, 2w/z. \tag{1015, 3}$$

According to the crude treatment of § 1007 this simplifies to

$$N_A(\chi_0 - \tfrac{3}{2}kT - \theta w), \tag{1015, 4}$$

while according to the refined treatment (3) becomes

$$N_A(\chi_0 - \tfrac{3}{2}kT) - N_S\, 2\bar{x}w, \tag{1015, 5}$$

with $\bar{x}$ given by (1010, 4). We can obtain the molecular energy of desorption by differentiating these formulae with respect to $N_A$ at constant $N_S$. In the absence of any independent estimate of $\chi_0$ and $w$ we cannot as yet make any practical use of these formulae.

As mentioned in § 1001 it is with respect to their isotherms that monolayers are particularly tractable, but as regards the temperature dependence of their properties they are even more complicated than interfaces between two phases of a single component. We shall conclude the chapter with a brief consideration of such interfaces.

**§ 1016. Energy and free energy of adhesion between liquid and vapour.** As an introduction to a discussion of the energy and free energy of a surface between a liquid and its vapour we shall derive formulae for the energy and free energy of adhesion of a column of the one phase to a column of the other, the two phases being divided by a plane surface. Since we can at the best obtain only rough formulae, we shall attempt to calculate only the contribution of the molecular attractions when each molecule is in an average position of minimum potential energy and shall entirely omit the contributions of the translations and internal degrees of freedom of the molecules. In other words we assume that the internal degrees of freedom and translational motion are the same for a molecule in the surface as in the interior of either bulk phase. This assumption is certainly not accurate, but

the inaccuracy thereby introduced is no worse than that due to various other approximations which we shall be unable to avoid. These several approximations are implicitly inherent in the classical discussions of Rayleigh* following those of Maxwell, Laplace and Young. The formulae which we shall derive are substantially those of Rayleigh in modern dress.

Consider a particular molecule at a point $P$ in the vapour phase, distant $f$ from a slab of uniform thickness $df$ in the liquid phase parallel to the surface dividing the liquid and vapour. From this slab dissect out that ring whose boundaries on the face nearer $P$ lie at distances $r$ and $r+dr$ from $P$. From Fig. 3 we see that the width of such a ring is $dr/\sin\theta$ and its radius is $r\sin\theta$. Its volume is therefore $2\pi r\,dr\,df$. If the average number of molecules per unit volume in this ring of slab is $n$, then the number of molecules in the slab is $n2\pi r\,dr\,df$. The value of $n$, when we know that there is a molecule at $P$, will in general be different from its value if $P$ were a point chosen at random, and its value may therefore depend on $r$ as well as $f$. If $\epsilon(r)$ denotes the interaction energy of a pair of molecules distant $r$ apart (averaged if necessary over all orientations), then the energy of interaction between the molecule at $P$ and the molecules in the ring is

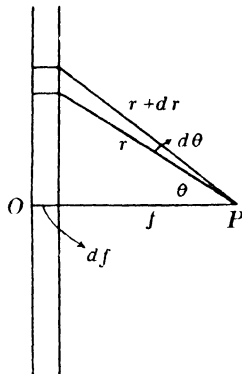



Fig. 3.

$$n2\pi r\,\epsilon(r)\,dr\,df. \qquad (1016, 1)$$

The corresponding average force attracting the molecule at $P$ towards the plane of the ring is

$$n2\pi r\frac{f}{r}\frac{\partial\epsilon}{\partial r}dr\,df. \qquad (1016, 2)$$

The interaction energy between the molecule at $P$ and the molecules in the whole slab is

$$2\pi\,df\int_f^\infty n\epsilon(r)\,r\,dr, \qquad (1016, 3)$$

and the corresponding force of attraction

$$2\pi f\,df\int_f^\infty n\frac{\partial\epsilon}{\partial r}dr. \qquad (1016, 4)$$

The interaction energy between the molecule at $P$ in the vapour and the molecules in a semi-infinite volume of liquid bounded by a plane surface distant $j$ from $P$ is

$$2\pi\int_j^\infty df\int_f^\infty n\epsilon(r)\,r\,dr, \qquad (1016, 5)$$

* Rayleigh, *Scientific Papers*, 3, 397 (1890).

and the corresponding force of attraction

$$2\pi \int_j^\infty f\,df \int_f^\infty n \frac{\partial \epsilon}{\partial r} dr. \qquad (1016, 6)$$

For each slab in the liquid $n$ now depends on $j$ as well as on $f$ and on $r$.

Let us now replace the molecule at $P$ by a slab of vapour of area $A$, of thickness $dj$ parallel to the surface of the liquid and at a distance $j$ from it. If the number of molecules per unit volume in this slab of vapour is $n'$, then the average interaction energy between this slab and the semi-infinite volume of liquid is

$$2\pi A n' dj \int_j^\infty df \int_f^\infty n\epsilon(r)\, r\, dr, \qquad (1016, 7)$$

and the corresponding force of attraction

$$2\pi A n' dj \int_j^\infty f\,df \int^\infty n \frac{\partial \epsilon}{\partial r} dr. \qquad (1016, 8)$$

The interaction energy between all the molecules in a semi-infinite column of vapour, whose cross-section is of area $A$ and whose flat base is distant $z$ from the face of the semi-infinite volume of liquid, is

$$2\pi A \int_z^\infty n' dj \int_j^\infty df \int_f^\infty n\epsilon(r)\, r\, dr, \qquad (1016, 9)$$

and the corresponding force of attraction

$$2\pi A \int_z^\infty n' dj \int_j^\infty f\,df \int_f^\infty n \frac{\partial \epsilon}{\partial r} dr. \qquad (1016, 10)$$

We can derive the total energy of adhesion $E^{\mathrm{adh}}$ between liquid and vapour across an area $A$ by setting $z = 0$ in (9). We obtain

$$E^{\mathrm{adh}} = 2\pi A \int_0^\infty n' dj \int_j^\infty df \int_f^\infty n\epsilon(r)\, r\, dr. \qquad (1016, 11)$$

We can similarly derive the free energy $F^{\mathrm{adh}}$ of adhesion between liquid and vapour across an area $A$ by multiplying (10) by $dz$ and integrating from 0 to $\infty$. We thus obtain

$$F^{\mathrm{adh}} = 2\pi A \int_0^\infty dz \int_z^\infty n' dj \int_j^\infty f\,df \int_f^\infty n \frac{\partial \epsilon}{\partial r} dr. \qquad (1016, 12)$$

The zero of free energy is here taken as that for the liquid and vapour phases at infinite separation, each having a free surface $A$ in contact with a vacuum. This zero is distinctly artificial but this does not matter, as the choice of zero always is eliminated when we compare the free energy of any two actually occurring states.

Formulae (11) and (12) are equally accurate, even if not equally useful, provided care is taken to insert the correct values of $n$ and $n'$. In applying

(11) to a liquid-vapour interface we may usually with sufficient accuracy ignore any dependence of $n$ and $n'$ on $r$, and regard $n$ as a function only of $f-j$, the distance of the element of liquid from the interface, and $n'$ as a function only of $j$, the distance of the element of vapour from the interface between liquid and vapour. We therefore write

$$E^{\mathrm{adh}} = 2\pi A \int_0^\infty n'(j)\,dj \int_j^\infty df \int_f^\infty n(f-j)\,\epsilon(r)\,r\,dr. \quad (1016, 13)$$

In (12) on the other hand $n$ and $n'$, as well as depending on $f$ and $j$, will also depend on $z$, the distance between the free surface of the liquid and that of the vapour. We therefore write

$$F^{\mathrm{adh}} = 2\pi A \int_0^\infty dz \int_z^\infty n'(j,z)\,dj \int_j^\infty f\,df \int_f^\infty n(f-j,z)\,\frac{\partial\epsilon}{\partial r}\,dr. \quad (1016, 14)$$

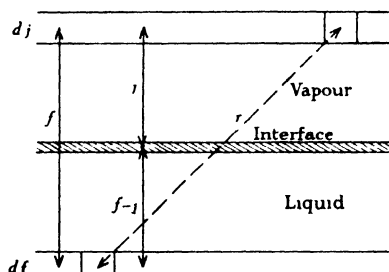



Fig. 4*a*.

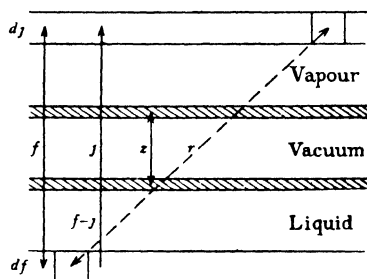



Fig. 4*b*.

The variables occurring in formulae (13) and (14) are shown in Figs. 4*a* and 4*b* respectively. In each case equilibrium values of $n$ and $n'$ have to be used. The use of (14) therefore implies the presence of ideal walls to separate the liquid and vapour phases from the vacuum. These ideal walls must have no configurational interaction energy with the molecules and merely reverse the momentum of the molecules normal to the wall. It is considerably more difficult to estimate the dependence of $n$ and $n'$ on $z$ (as well as on $f$ and $j$) in Fig. 4*b* than to estimate that of $n$ and $n'$ on $f$ and $j$ in Fig. 4*a*. Formula (13) is thus considerably easier to apply than (14). We shall therefore use (13) to estimate the total energy, but instead of using (14) shall determine $F^{\mathrm{adh}}$ by means of the thermodynamic relation

$$\frac{\partial(F^{\mathrm{adh}}/T)}{\partial T} = -\frac{E^{\mathrm{adh}}}{T^2}. \quad (1016, 15)$$

**§ 1017. Surface energy of liquid-vapour interface.** According to the definition of surface energy, we can compute the surface energy per area $A$ of a liquid-vapour interface as the sum of the energy increases in

three processes: (i) breaking apart a column of liquid of cross-section $\frac{1}{2}A$; (ii) breaking apart a similar column of vapour; (iii) putting together the two pairs of liquid-vapour columns. We use (1016, 13) for the energy of adhesion of vapour to liquid. For the energy of adhesion of liquid to liquid across an area $A$ we have the analogous formula

$$2\pi A n_0^2 \int_0^\infty dj \int_j^\infty df \int_f^\infty \epsilon(r)\, r\, dr, \qquad (1017, 1)$$

where $n_0$ is the uniform value of $n$ in the interior of the liquid. Similarly for the energy of adhesion of vapour to vapour across an area $A$ we shall use

$$2\pi A n_0'^2 \int_0^\infty dj \int_j^\infty df \int_f^\infty \epsilon(r)\, r\, dr, \qquad (1017, 2)$$

where $n_0'$ is the uniform value of $n'$ in the interior of the vapour. This ignores the dependence of $n'$ on $r$ in (1016, 11) in the vapour, but the term is small and we shall be content to ignore this refinement. The energies of adhesion given by (1), (2) and (1016, 13) are, like $\epsilon(r)$ for important values of $r$, all negative. Using these formulae we obtain for $E^S$, the surface energy for an area $A$ of liquid-vapour interface,

$$\begin{aligned}\frac{E^S}{A} = &-\pi n_0^2 \int_0^\infty dj \int_j^\infty df \int_f^\infty \epsilon(r)\, r\, dr \\ &-\pi n_0'^2 \int_0^\infty dj \int_j^\infty df \int_f^\infty \epsilon(r)\, r\, dr \\ &+ 2\pi \int_0^\infty n'(j)\, dj \int_j^\infty n(f-j)\, df \int_f^\infty \epsilon(r)\, r\, dr. \end{aligned} \qquad (1017, 3)$$

As yet the problem of the molecular distribution in the neighbourhood of an interface has not been seriously attacked, much less solved. We are therefore compelled to make crude approximations concerning $n(f-j)$ and $n'(j)$. The obvious approximation is to set

$$n(f-j) = n_0, \qquad (1017, 4)$$

$$n'(j) = n_0'. \qquad (1017, 5)$$

This corresponds to the assumption that the molecular density in the liquid and that in the vapour both remain constant right up to a geometrical plane, at which there is a sharp discontinuity. It is difficult to estimate the inaccuracy due to this approximation. Substituting from (4) and (5) into (3), we obtain

$$\frac{E^S}{A} = -(n_0' - n_0)^2 \pi \int_0^\infty dj \int_j^\infty df \int_f^\infty \epsilon(r)\, r\, dr. \qquad (1017, 6)$$

If we integrate by parts twice we obtain the simpler formula

$$\frac{E^S}{A} = -(n'-n)^2 \tfrac{1}{2}\pi \int_0^\infty \epsilon(r)\, r^3 dr, \tag{1017, 7}$$

dropping the subscripts 0 which are no longer necessary.

**§ 1018. Surface tension near the critical point.** Since at the critical temperature $T_c$ both $F^S$ and $E^S$ must vanish, we can write the thermodynamic relation

$$\frac{\partial(F^S/T)}{\partial T} = -\frac{E^S}{T^2} \tag{1018, 1}$$

in the integrated form

$$F^S = T\int_T^{T_c} \frac{E^S}{T^2}\, dT. \tag{1018, 2}$$

To use (2) we require to know $E^S$ as a function of $T$, whereas according to (1017, 7) we have $E^S$ as a function of $(n'-n)$. However, it was pointed out in § 729 that *in the immediate neighbourhood of the critical point* one has the approximate functional relationship

$$(n'-n)^2 \propto T_c - T. \tag{1018, 3}$$

We have therefore in the immediate neighbourhood of the critical point, according to (1017, 7) and (3)

$$E^S/A = a(n'-n)^2 = b(T_c - T), \tag{1018, 4}$$

where

$$a = -\tfrac{1}{2}\pi \int_0^\infty \epsilon(r)\, r^3 dr > 0, \tag{1018, 5}$$

and $b$ is another positive constant. Since (4) is correct only to the first order in $T_c - T$, we replace (2) by the simpler approximation

$$F^S = \frac{1}{T_c}\int_T^{T_c} E^S\, dT, \tag{1018, 6}$$

which is also correct to the first order in $T_c - T$. Substituting from (4) into (6) and performing the integration, we obtain for the surface tension $\gamma$

$$\gamma = \frac{F^S}{A} = \frac{1}{T_c}\int_T^{T_c} b(T_c - T)\, dT = \frac{b}{2T_c}(T_c - T)^2$$

$$= \frac{a^2}{2bT_c}(n'-n)^4. \tag{1018, 7}$$

It has been shown by Macleod* that the empirical relation

$$\gamma \propto (n'-n)^4 \tag{1018, 8}$$

represents with satisfactory accuracy the behaviour of the surface tension

* Macleod, *Trans. Fara. Soc.* **19**, 38 (1923).

of many substances over the whole experimental range from the critical point down to the freezing-point. That it has proved possible to derive a functional relation of the form (8) *for the immediate neighbourhood of the critical point* is therefore satisfactory. As soon as we leave this region, however, both the approximations (4) and (6), required in the derivation of (7), become inaccurate. The validity of Macleod's relation over a wider temperature range must therefore, at least for the present, be regarded as due to accidental compensation of several factors.*

* For a more detailed discussion of the theoretical basis of Macleod's relation, see Fowler, *Proc. Roy. Soc.* A, **159**, 229 (1937).

# CHAPTER XI

## ELEMENTARY ELECTRON THEORY OF METALS

**§ 1100. Introduction.** The modern elementary theory of a metal was originated by Sommerfeld,* who inserted the necessary quantal corrections into the classical theory of Drude† and Lorentz.‡ To a first approximation one may assume that the long-range effects of the electronic charges in the metal are neutralized by the charges of the heavy atomic ions. In this approximation we entirely neglect the internal structure of the metal and regard it merely as a home for electrons, where they can move freely in a region of uniform potential energy.

On this model the properties of the metal are defined by its temperature, its volume, the number $N$ of free electrons, and the potential energy $-\chi_0$ of a free electron, whose potential energy in free space just outside the metal is taken to be zero. The question immediately arises how many of the electrons are to be regarded as free. The answer is that, as the treatment of the free electrons as moving in a region of uniform potential is at the best only a crude approximation, the choice of how many of the electrons are to be treated as free is largely arbitrary. Evidently the more tightly an electron is bound the worse is the approximation of motion in a region of uniform potential. It would therefore be a bad approximation to treat all the electrons as free. Since, however, all the atoms are on the same footing, we might expect a definite number of free electrons per atom We can reasonably assume either one electron per atom or all the normal valency electrons as effectively free. The choice made is not very important, as it has little effect on the final results, a deeper treatment removes this arbitrary feature and enables a rational choice to be made. The simple theory applies best to the alkali metals, and somewhat less well to the noble metals, assuming one free electron per atom.

As already mentioned, the free electrons are assumed to move in a region of uniform potential energy $-\chi_0$, their potential energy in free space just outside the metal being taken as zero. It is a fundamental assumption of Sommerfeld's treatment that $\chi_0$ is independent of the temperature. We shall investigate the conclusions deducible from this assumption, and later in § 1118 return to a discussion of its validity. Actually we are almost entirely ignorant of how $\chi_0$ should depend theoretically on the temperature. We may

* Sommerfeld, *Zeit. Phys.* **47**, 1 (1928)

† Drude, *Ann d. Phys* **1**, 566, **3**, 369 (1900).

‡ Lorentz, *The Theory of Electrons* (Teubner, 1916), especially note 29

hope that the assumption of temperature independence may be a not too bad approximation, but at present it can be justified only by comparison between the predictions of the theory and the results of experiment.

Considerable progress has been made in the analysis of the electronic levels in metals, taking into account the discrete atomic structure.* This confirms Sommerfeld's treatment of free electrons as a useful first approximation. We shall refer to the more refined theory only briefly in §§ 1108-1110 and shall otherwise confine ourselves entirely to Sommerfeld's approximation of free electrons. We give this in considerable detail as the best simple example of the use of Fermi-Dirac statistics.

§ **1101. Statistics of electron gas.** We recall that electrons obey strictly the Fermi-Dirac statistics, according to which, out of a total of $N$ electrons, the number $n_r$ in the state $r$ of energy $\epsilon_r$ and weight $\varpi_r$ is given by

$$n_r = \frac{\varpi_r}{1 + e^{\epsilon_r/kT}/\lambda}, \tag{1101,1}$$

where $\lambda$ is determined by the necessary condition

$$\Sigma_r n_r = N. \tag{1101,2}$$

When it happens that the condition

$$\lambda \ll e^{\epsilon_0/kT} \tag{1101,3}$$

is satisfied, (1) and (2) reduce to

$$\lambda \Sigma_r \varpi_r e^{-\epsilon_r/kT} = N. \tag{1101,4}$$

We thus have
$$n_r = \frac{\varpi_r e^{-\epsilon_r/kT}}{\Sigma_r \varpi_r e^{-\epsilon_r/kT}} = \frac{\varpi_r e^{-\epsilon_r/kT}}{f(T)}, \tag{1101,5}$$

where $f(T)$ is the ordinary partition function. Formula (5) is the fundamental distribution law of classical statistics, while (3) is the general condition that either Fermi-Dirac or Bose-Einstein statistics should reduce to classical statistics.

We recall that in Chapter II we tentatively assumed (3) to be true, deduced the consequences including the evaluation of $\lambda$ and so could verify the correctness of our assumption. We found that the condition (3) is satisfied even for the least favourable case of a perfect gas of light molecules at low temperatures, such as helium gas at 1° K. Deviations would appear at high pressures, but these would be less important than the deviations from the ideal gas laws due to the intermolecular attractions. It was mentioned that the one important terrestrial example of the failure of the condition (3) is for free electrons in metals. Owing to the breakdown of (3), we may not

* For a comprehensive discussion see Mott and Jones, *Properties of Metals and Alloys* (Oxford, 1936) and *S M* Chapter XI.

use the approximation of classical statistics for free electrons in metals, but must apply the strict Fermi-Dirac formula (1). The failure of (3) is due to the mass of the electron being so much smaller than that of any atom or molecule. The failure of (3) is so extreme for free electrons in metals that we actually have the opposite condition,

$$\lambda \gg e^{\epsilon_0/kT} \qquad (1101, 6)$$

obeyed even at temperatures as high as 2000° K. We shall assume (6) to be satisfied, shall deduce the consequences and evaluate $\lambda$; we can then verify that the assumption was justified.

We may mention here that the density of electrons in the vapour phase in equilibrium with a metal is so very small, that in spite of the low mass of the electron the condition (3) is fulfilled in the vapour phase. If then we take as zero the energy of an electron at rest in the vapour, we have in the vapour phase the usual formula for a perfect gas

$$\lambda = \frac{N}{V}\frac{h^3}{2(2\pi m_e kT)^{\frac{3}{2}}}, \qquad (1101, 7)$$

where $m_e$ is the mass of the electron, and the factor 2 in the denominator is the weight factor for the two possible directions of electron spin. When we have evaluated $\lambda$ for the electrons in the metal, the equilibrium concentration of electrons in the vapour phase will be given by equating the values of $\lambda$ in the metal and vapour.

**§ 1102. Detailed formulae for an electron gas.** We have to determine $\lambda$ so as to satisfy simultaneously (1101, 1) and (1101, 2). In other words we have to solve for $\lambda$ the equation

$$N = \Sigma_r \frac{\varpi_r}{1 + e^{\epsilon_r/kT}/\lambda}. \qquad (1102, 1)$$

It is convenient initially to take as energy zero an electron at rest inside the metal. It is easy to transform to any other energy zero at a later stage. We shall initially assume

$$\lambda \gg 1, \qquad (1102, 2)$$

since $\epsilon_0$ is now zero, and shall have to verify this *a posteriori*.

The first step is the enumeration of the energy values. On referring to § 219 we recall that a point mass in a rectangular box with sides $a$, $b$, $c$ has quantum states characterized by quantum numbers $l$, $m$, $n$ which can each take all positive integral (non-zero) values. The energy values are given by

$$\epsilon_{l,m,n} = \frac{h^2}{8m_e}\left(\frac{l^2}{a^2} + \frac{m^2}{b^2} + \frac{n^2}{c^2}\right). \qquad (1102, 3)$$

For point masses these states are non-degenerate, but for electrons each of these states has a weight $\varpi_{l,m,n} = 2$, owing to the electron spin.

It is now convenient to collect together all states of equal energy. All states of energy $\epsilon_r$ have values of $l$, $m$, $n$ lying on the surface of the positive octant of the ellipsoid

$$\frac{l^2}{a^2}+\frac{m^2}{b^2}+\frac{n^2}{c^2} = \frac{8m_e\epsilon_r}{h^2}, \tag{1102, 4}$$

and so all states with energy less than or equal to $\epsilon_r$ have values of $l$, $m$, $n$ inside the positive octant of this ellipsoid. But the number of points with integral coordinates $l$, $m$, $n$ within this octant is effectively equal to the volume of the octant, namely

$$\frac{\pi}{6}\left(\frac{8m_e\epsilon_r}{h^2}\right)^{\frac{3}{2}} abc = \frac{\pi}{6}\frac{(8m_e\epsilon_r)^{\frac{3}{2}}}{h^3} V, \tag{1102, 5}$$

where $V$ is the volume of the enclosure. It has been proved that the validity of (5) is independent of the shape of the enclosure. The number of electronic states of energy less than or equal to $\epsilon_r$ is owing to the electron spin just double this, namely

$$2\frac{\pi}{6}\frac{(8m_e\epsilon_r)^{\frac{3}{2}}}{h^3} V. \tag{1102, 6}$$

To obtain the number of electronic states with energies in the range $\epsilon_r$ to $\epsilon_r + d\epsilon_r$ we differentiate (6) and obtain

$$2\frac{\pi}{4}\frac{(8m_e)^{\frac{3}{2}}}{h^3} V\epsilon_r^{\frac{1}{2}}\,d\epsilon_r. \tag{1102, 7}$$

If we treat all these states as a single degenerate state of energy $\epsilon_r$, then the expression (7) becomes the appropriate weight $\varpi_r$. Substituting this value for $\varpi_r$ into (1) and replacing the sum by an integral, we obtain

$$N = 2\frac{\pi}{4}\frac{(8m_e)^{\frac{3}{2}}}{h^3} V\int_0^\infty \frac{\epsilon^{\frac{1}{2}}\,d\epsilon}{1+e^{\epsilon/kT}/\lambda}$$

$$= 2\frac{\pi}{4}\frac{(8m_e kT)^{\frac{3}{2}}}{h^3} V\int_0^\infty \frac{x^{\frac{1}{2}}\,dx}{1+e^{x}/\lambda}. \tag{1102, 8}$$

It is convenient for the sake of brevity to introduce a characteristic energy $\epsilon^*$, such that the number of states of energy not greater than $\epsilon^*$ is just equal to the total number $N$ of free electrons. Using (6) we see that $\epsilon^*$ thus defined is given by

$$\frac{N}{V} = 2\frac{\pi}{6}\frac{(8m_e\epsilon^*)^{\frac{3}{2}}}{h^3}, \tag{1102, 9}$$

or by

$$\epsilon^* = \frac{h^2}{8m_e}\left(\frac{3N}{\pi V}\right)^{\frac{2}{3}}. \tag{1102, 10}$$

We note that $\epsilon^*$ is determined by the electron concentration $N/V$ and is, for given $N/V$, independent of the temperature.

Substituting from (9) into (8) we obtain

$$1 = \left(\frac{kT}{\epsilon^*}\right)^{\frac{3}{2}}\frac{3}{2}\int_0^\infty \frac{x^{\frac{1}{2}}\,dx}{1+e^{x}/\lambda}. \tag{1102, 11}$$

To obtain an expression for the average kinetic energy $E^{\text{kin}}$ of the electrons we have to include an extra factor $\epsilon$ in the integral of (9). We thus have

$$E^{\text{kin}} = 2\frac{\pi}{4}\frac{(8m_e)^{\frac{3}{2}}}{h^3}V\int_0^{\infty}\frac{\epsilon^{\frac{3}{2}}\,d\epsilon}{1+e^{\epsilon/kT}/\lambda}$$

$$= 2\frac{\pi}{4}\frac{(8m_e kT)^{\frac{3}{2}}\,kT}{h^3}V\int_0^{\infty}\frac{x^{\frac{3}{2}}\,dx}{1+e^{x}/\lambda}. \qquad (1102, 12)$$

Using the definition (9) of $\epsilon^*$, we can write this as

$$\frac{E^{\text{kin}}}{N} = \left(\frac{kT}{\epsilon^*}\right)^{\frac{3}{2}}\tfrac{3}{2}kT\int_0^{\infty}\frac{x^{\frac{3}{2}}\,dx}{1+e^{x}/\lambda}. \qquad (1102, 13)$$

If we can evaluate the integrals (11) and (13), either exactly† or approximately, we shall obtain one relation between $\epsilon^*$ and $\lambda$ and another relation between $E^{\text{kin}}/N$, $\epsilon^*$ and $\lambda$. If we can eliminate $\lambda$ between these, we shall obtain $E^{\text{kin}}/N$ as a function of $\epsilon^*$ that is to say of $N/V$.

**§ 1103. First approximation and numerical values for $\lambda$.** It is easy to obtain a first approximation to the integral

$$\int_0^{\infty}\frac{x^{\frac{1}{2}}\,dx}{1+e^{x}/\lambda}, \qquad (1103, 1)$$

occurring in (1102, 11). For we notice that for $x \ll \log\lambda$ the integrand is effectively $x^{\frac{1}{2}}$, while for $x \gg \log\lambda$ the integrand becomes very small We can therefore obtain a first approximation to the integral by using the approximations

$$\left.\begin{aligned}\frac{x^{\frac{1}{2}}}{1+e^{x}/\lambda} &\simeq x^{\frac{1}{2}} \quad (x<\log\lambda)\\ \frac{x^{\frac{1}{2}}}{1+e^{x}/\lambda} &\simeq 0 \quad (x>\log\lambda)\end{aligned}\right\}. \qquad (1103, 2)$$

This approximation appears at first sight extremely crude, but we shall actually find later that it is quite a good approximation, and actually sufficient for most purposes. At all events it is adequate for verifying (1102, 2). Using the approximation (2) the integral (1) reduces to

$$\int_0^{\log\lambda} x^{\frac{1}{2}}\,dx = \tfrac{2}{3}(\log\lambda)^{\frac{3}{2}}. \qquad (1103, 3)$$

Substituting this approximation into (1102, 11) we obtain

$$1 = \left(\frac{kT\log\lambda}{\epsilon^*}\right)^{\frac{3}{2}}, \qquad (1103, 4)$$

or

$$\log\lambda = \epsilon^*/kT. \qquad (1103, 5)$$

† Accurate values of these integrals for all values of $\lambda$ have been calculated and tabulated by McDougall and Stoner, *Phil. Trans. Roy. Soc.* **237**, 67 (1938).

Inserting numerical values for $h$, $m_e$, $k$ into (1102, 10), we obtain

$$\epsilon^*/k = 4{\cdot}2 \times 10^5 \left(\frac{N}{V}\right)^{\frac{2}{3}} \text{deg.} \quad (N/V \text{ in electrons/Å}^3). \qquad (1103, 6)$$

For copper, whose density is 8·9 and atomic weight 63, the atomic volume is about 12 Å$^3$ Assuming one free electron per atom, we obtain for copper

$$\epsilon^*/k \simeq 8 \times 10^4 \,\text{deg.} \qquad (1103, 7)$$

Using this value in (5) we see therefore that $\log\lambda$ is still 80 at 1000° K. and 40 at 2000° K., amply large enough for the use of the foregoing approximations. For caesium, in which the atomic density has the lowest value known for a metal, $N/V$ is less by a factor of 10 and $\log\lambda$ by a factor of 5, but $\log\lambda$ is still large enough for the application of these formulae at any temperature below the melting-point of caesium. For any solid metal therefore we may normally expect (1102, 2) to be satisfied.

The same approximation, which leads to the value (3) for the integral (1), gives us

$$\int_0^\infty \frac{x^{\frac{1}{2}}\,dx}{1+e^x/\lambda} = \int_0^{\log\lambda} x^{\frac{1}{2}}\,dx = \tfrac{2}{3}(\log\lambda)^{\frac{3}{2}}. \qquad (1103, 8)$$

Substituting (8) into (1102, 13) and using (5), we obtain for the average kinetic energy of an electron in the metal

$$\frac{E^{\text{kin}}}{N} = \left(\frac{kT}{\epsilon^*}\right)^{\frac{3}{2}} \tfrac{3}{2}kT \frac{2}{5}\left(\frac{\epsilon^*}{kT}\right)^{\frac{5}{2}} = \tfrac{3}{5}\epsilon^*. \qquad (1103, 9)$$

**§ 1104. Second approximation for $\lambda$.** We shall now derive a better approximation to the integral

$$I = \int_0^\infty \frac{x^{\frac{1}{2}}\,dx}{1+e^x/\lambda}. \qquad (1104, 1)$$

We first integrate by parts, obtaining

$$I = \frac{1}{2}\int_0^\infty x^{-\frac{1}{2}} \log(1+\lambda e^{-x})\,dx = \frac{1}{2}\int_0^\infty x^{-\frac{1}{2}} \log(1+e^{\beta-x})\,dx, \qquad (1104, 2)$$

where

$$\beta = \log\lambda. \qquad (1104, 3)$$

We now break the range of integration at $x = \beta$ and obtain

$$\begin{aligned} 2I &= \int_0^\beta x^{-\frac{1}{2}} \log(1+e^{\beta-x})\,dx + \int_\beta^\infty x^{-\frac{1}{2}} \log(1+e^{\beta-x})\,dx \\ &= \int_0^\beta x^{-\frac{1}{2}}(\beta-x)\,dx + \int_0^\beta x^{-\frac{1}{2}} \log(1+e^{x-\beta})\,dx + \int_\beta^\infty x^{-\frac{1}{2}} \log(1+e^{\beta-x})\,dx \\ &= \int_0^\beta x^{-\frac{1}{2}}(\beta-x)\,dx + \int_0^\beta (\beta-y)^{-\frac{1}{2}} \log(1+e^{-y})\,dy \\ &\qquad + \int_0^\infty (\beta+y)^{-\frac{1}{2}} \log(1+e^{-y})\,dy. \end{aligned} \qquad (1104, 4)$$

In the last two integrals, the logarithms can be expanded, giving

$$2I = \int_0^\beta x^{-\frac{1}{2}}(\beta - x)\,dx + \sum_{s=1}^{\infty} \frac{(-)^{s-1}}{s} \int_0^\beta e^{-sy}(\beta - y)^{-\frac{1}{2}}\,dy$$
$$+ \sum_{s=1}^{\infty} \frac{(-)^{s-1}}{s} \int_0^\infty e^{-sy}(\beta + y)^{-\frac{1}{2}}\,dy. \qquad (1104, 5)$$

This is exact. When $\beta$ is large the square roots in the last two integrands can both be replaced by $\beta^{-\frac{1}{2}}$ to give the dominant terms. The range of the integrals of the first series can then be extended to infinity without sensible error. Thus approximately

$$I = \frac{1}{2}\int_0^\infty x^{-\frac{1}{2}}(\beta - x)\,dx + \beta^{-\frac{1}{2}} \sum_{s=1}^{\infty} \frac{(-)^{s-1}}{s} \int_0^\infty e^{-sy}\,dy$$
$$= \tfrac{2}{3}\beta^{\frac{3}{2}} + \frac{\pi^2}{12}\beta^{-\frac{1}{2}} = \tfrac{2}{3}(\log\lambda)^{\frac{3}{2}} + \frac{\pi^2}{12}(\log\lambda)^{-\frac{1}{2}}. \qquad (1104, 6)$$

The method can be extended to show that the error term is $O(\log\lambda)^{-\frac{5}{2}}$ or to give a general asymptotic expansion in powers of $(\log\lambda)^{-2}$.

Substituting (6) into (1102, 11), we obtain

$$\left(\frac{\epsilon^*}{kT}\right)^{\frac{3}{2}} = (\log\lambda)^{\frac{3}{2}} + \frac{\pi^2}{8}(\log\lambda)^{-\frac{1}{2}}. \qquad (1104, 7)$$

We can solve (7) for $\log\lambda$ by successive approximations. As a first approximation, retaining only the first term on the right, we obtain

$$\log\lambda = \epsilon^*/kT, \qquad (1104, 8)$$

confirming (1103, 5). Substituting this value of $\log\lambda$ in the second order terms in (7), we obtain as the second approximation

$$\log\lambda = \frac{\epsilon^*}{kT}\left\{1 - \frac{\pi^2}{12}\left(\frac{kT}{\epsilon^*}\right)^2\right\}. \qquad (1104, 9)$$

We have already seen that for copper $\epsilon^*/k = 8\times10^4$ deg., so that at 1000° K. the second term in the bracket is only about $(1/80)^2$. We conclude that the first approximation (8) is remarkably accurate, and we shall hardly ever require to use the more exact formula (9).

We can apply precisely the same method, which led to (6), to obtain an approximate evaluation of the integral occurring in (1102, 13). We thus obtain

$$\int_0^\infty \frac{x^{\frac{3}{2}}\,dx}{1+e^{x-\beta}} = \frac{3}{2}\int_0^\infty x^{\frac{1}{2}}\log(1+e^{\beta-x})\,dx$$
$$= \frac{3}{2}\int_0^\beta x^{\frac{1}{2}}(\beta - x)\,dx + 3\beta^{\frac{1}{2}} \sum_{s=1}^{\infty} \frac{(-)^{s-1}}{s} \int_0^\infty e^{-sy}\,dy$$
$$= \tfrac{2}{5}\beta^{\frac{5}{2}} + \frac{\pi^2}{4}\beta^{\frac{1}{2}}. \qquad (1104, 10)$$

Using this in (1102, 13) we obtain for the average kinetic energy

$$\frac{E^{\text{kin}}}{N} = \left(\frac{kT}{\epsilon^*}\right)^{\frac{5}{2}} \tfrac{3}{5}kT(\log\lambda)^{\frac{5}{2}}\left\{1+\frac{5\pi^2}{8}(\log\lambda)^{-2}\right\}. \qquad (1104, 11)$$

If we substitute into (11) the value of $\log\lambda$ given by (9), we obtain

$$\frac{E^{\text{kin}}}{N} = \tfrac{3}{5}\epsilon^*\left\{1-\tfrac{5}{2}\frac{\pi^2}{12}\left(\frac{kT}{\epsilon^*}\right)^2\right\}\left\{1+\frac{5\pi^2}{8}\left(\frac{kT}{\epsilon^*}\right)^2\right\} = \tfrac{3}{5}\epsilon^*\left\{1+\frac{5\pi^2}{12}\left(\frac{kT}{\epsilon^*}\right)^2\right\}, \qquad (1104, 12)$$

neglecting higher powers of $(kT/\epsilon^*)$. Formula (1103, 9) is a good approximation to (12).

**§ 1105. Distribution of velocities.** According to (301, 19), the range $d|p_x|$ of the magnitude of the $x$-component of the momentum of a particle in a box corresponds to the range $2a\,d|p_x|/h$ of the quantum number $l$. Hence the element $d|p_x|\,d|p_y|\,d|p_z|$ of momentum space includes

$$8abc\,d|p_x|\,d|p_y|\,d|p_z|/h^3 = 8V\,d|p_x|\,d|p_y|\,d|p_z|/h^3$$

translational states or, taking account of electron spin,

$$16V\,d|p_x|\,d|p_y|\,d|p_z|/h^3$$

quantum states in all. Now provided we do not try to define the position of an electron too exactly, we may legitimately regard half the electrons as having $p_x$ positive and the other half as having $p_x$ negative, and similarly for $p_y$, $p_z$. We therefore assign to the element $dp_x dp_y dp_z$ of momentum space one-eighth as many quantum states as to the element $d|p_x|\,d|p_y|\,d|p_z|$, that is $2V\,dp_x dp_y dp_z/h^3$ in all. This might have been derived more simply, but less convincingly, by classical reasoning and use of the limiting principle. Using then the value

$$2V\,dp_x dp_y dp_z/h^3 \qquad (1105, 1)$$

for the weight factor in (1102, 1), we obtain for the average number of electrons with momentum components in the element of momentum space $dp_x dp_y dp_z$

$$\frac{2V}{h^3}\frac{dp_x dp_y dp_z}{1+e^{\epsilon/kT}/\lambda}, \qquad (1105, 2)$$

where $\epsilon$ is the total kinetic energy given by

$$\epsilon = \tfrac{1}{2}(p_x^2+p_y^2+p_z^2)/m_e. \qquad (1105, 3)$$

According to the approximation (1104, 8) for $\lambda$, (2) becomes

$$\frac{2V}{h^3}\frac{dp_x dp_y dp_z}{1+e^{(\epsilon-\epsilon^*)/kT}}. \qquad (1105, 4)$$

The factor $\{1+e^{(\epsilon-\epsilon^*)/kT}\}^{-1}$, which is characteristic of Fermi-Dirac statistics, is shown plotted against $(\epsilon-\epsilon^*)$ for various values of $T$ in Fig. 1.

For the number $n(p_x)\,dp_x$ of electrons, with momentum in the $x$-direction in the range $dp_x$, incident on unit area normal to the $x$-axis per unit time, we have

$$n(p_x)\,dp_x = \frac{2}{h^3}\frac{p_x}{m_e}\,dp_x \int_{-\infty}^{+\infty} dp_y \int_{-\infty}^{+\infty} dp_z \frac{1}{1+e^{\epsilon/kT}/\lambda}, \qquad (1105, 5)$$

where $\epsilon$ is given by (3). The double integral gives the number of such electrons per unit volume and $p_x/m_e$ is their velocity of approach to the surface.

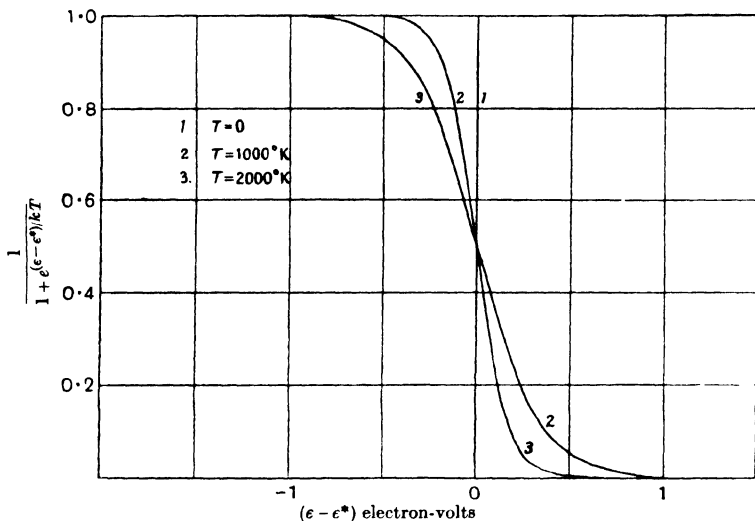



Fig. 1. The Fermi-Dirac factor $\{1+e^{(\epsilon-\epsilon^*)/kT}\}^{-1}$ as a function of $\epsilon-\epsilon^*$ for various values of $T$.

If we substitute

$$p_\rho^2 = p_y^2 + p_z^2, \qquad (1105, 6)$$

we obtain

$$n(p_x)\,dp_x = \frac{2p_x dp_x}{h^3 m_e}\int_0^\infty \frac{2\pi p_\rho\,dp_\rho}{1+e^{(p_x^2+p_\rho^2)/2m_e kT}/\lambda}$$

$$= \frac{4\pi m_e kT}{h^3}\frac{p_x dp_x}{m_e}\log(1+\lambda e^{-p_x^2/2m_e kT}). \qquad (1105, 7)$$

If $\zeta$ denotes the kinetic energy in the $x$-direction, then

$$2m_e\zeta = p_x^2, \quad m_e d\zeta = p_x dp_x, \qquad (1105, 8)$$

and the number $n(\zeta)\,d\zeta$ of electrons incident from one side on unit area per unit time with normal kinetic energy in the range $d\zeta$ is given by

$$n(\zeta)\,d\zeta = d\zeta\frac{4\pi m_e kT}{h^3}\log(1+\lambda e^{-\zeta/kT}); \qquad (1105, 9)$$

if we use the first approximation (1104, 8) to $\lambda$, this becomes

$$n(\zeta) = \frac{4\pi m_e kT}{h^3}\log\{1+e^{(\epsilon^*-\zeta)/kT}\}. \qquad (1105, 10)$$

This has the useful approximate form

$$n(\zeta) = \frac{4\pi m_e kT}{h^3} e^{-(\zeta-\epsilon^*)/kT} \quad (\zeta > \epsilon^*, \zeta - \epsilon^* \gg kT). \quad (1105, 11)$$

The function $n(\zeta)$ is shown plotted against $(\zeta - \epsilon^*)$ for various temperatures in Fig 2.

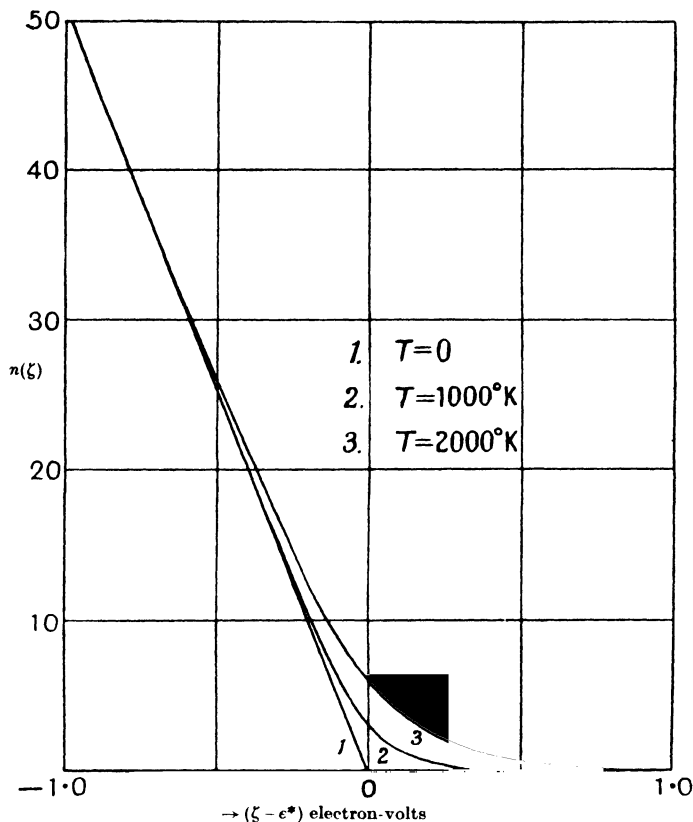



Fig 2. The number $n(\zeta)$ of electrons per unit range of energy incident on the boundary per cm.² per sec. as a function of $\zeta$ and $T$.

**§ 1106. Thermodynamic functions of an electron gas.** According to (224, 9) the partial potential is related to the absolute activity $\lambda$ by

$$\mu = kT \log \lambda. \quad (1106, 1)$$

Up to the present we have used as energy zero the state of an electron at rest inside the metal. This choice is of no significance as long as we confine

our attention to the inside of a single metal. If, however, we want to consider equilibria between a metal and the vapour phase, it becomes essential to use the same energy zero for both phases, and the most convenient zero is then the state of rest in the vapour. Changing to this zero, formula (1104, 9) for $\lambda$ becomes

$$\log \lambda = -\frac{\chi_0}{kT} + \frac{\epsilon^*}{kT} - \frac{\pi^2}{12}\frac{kT}{\epsilon^*}. \tag{1106, 2}$$

Substituting (2) into (1) we obtain for the partial potential $\mu_e$ of the electrons

$$\mu_e = -\chi_0 + \epsilon^* - \frac{\pi^2}{12}\frac{k^2T^2}{\epsilon^*}, \tag{1106, 3}$$

with the useful first approximation

$$\mu_e = -\chi_0 + \epsilon^*. \tag{1106, 4}$$

This formula tells us that the partial potential of an electron is equal to the energy separating the almost full states from the almost empty states. (Cf. Fig. 1.)

To obtain the free energy $F_e$ of the whole assembly of electrons we use the thermodynamic formula

$$F_e = \int_0^N \mu_e \, dN \quad (T, V \text{ constant}). \tag{1106, 5}$$

Substituting from (3) into (5) we obtain

$$F_e = \int_0^N \left\{ -\chi_0 + \epsilon^* - \frac{\pi^2}{12}\frac{k^2T^2}{\epsilon^*} \right\} dN \quad (T, V \text{ constant}). \tag{1106, 6}$$

Since according to (1102, 10)

$$\epsilon^* \propto N^{\frac{2}{3}} V^{-\frac{2}{3}}, \tag{1106, 7}$$

integration of (6), treating $\chi_0$ as independent of $N/V$, gives

$$\frac{F_e}{N} = -\chi_0 + \tfrac{3}{5}\epsilon^* - \frac{\pi^2}{4}\frac{k^2T^2}{\epsilon^*}. \tag{1106, 8}$$

For the total energy $E_e$ of the electrons we obtain

$$\frac{E_e}{N} = -T^2\left(\frac{\partial [F_e/T]}{\partial T}\right)_{N,V} = -\chi_0 + \tfrac{3}{5}\epsilon^* + \frac{\pi^2}{4}\frac{k^2T^2}{\epsilon^*}, \tag{1106, 9}$$

in agreement with (1104, 12).

We can also derive a formula for $P_e$, the pressure of the electrons. From (8) we deduce, using (7),

$$P_e = -\frac{\partial F_e}{\partial V} = \frac{2}{3}\frac{\epsilon^*}{V}\frac{\partial F_e}{\partial \epsilon^*} = \frac{N}{V}\left\{\tfrac{2}{5}\epsilon^* + \frac{\pi^2}{6}\frac{k^2T^2}{\epsilon^*}\right\}. \tag{1106, 10}$$

Comparing (10) with (9) we notice that

$$P_e V = \tfrac{2}{3}(E_e + N\chi_0) = \tfrac{2}{3}E_e^{\text{kin}}, \tag{1106, 11}$$

where $E_e^{\text{kin}}$ denotes the contribution of the kinetic energy to $E_e$. The relation (11) is in agreement with (603, 10) and confirms the virial theorem (706, 2).

We emphasized in § 301 that the relations between the energy $E$ of the assembly and the partial energy $\mathsf{E}$ of a single system are always related by

$$\mathsf{E} = \left(\frac{\partial E}{\partial N}\right)_{T,P} = \frac{E}{N}, \tag{1106, 12}$$

but that

$$\mathsf{E} \neq \left(\frac{\partial E}{\partial N}\right)_{T,V}, \tag{1106, 13}$$

except in the special case of a classical perfect gas. As there has been confusion of this point, it is of interest to verify these relations for an electron gas. Since according to (10) $P_e$ is determined completely by $T$, $V$, $\epsilon^*$, while $\epsilon^*$ is determined completely by $V$, we may replace (12) by

$$\mathsf{E} = \left(\frac{\partial E}{\partial N}\right)_{T,\epsilon^*}. \tag{1106, 14}$$

Using (9) and (14) and treating $\chi_0$ as constant, as assumed, we immediately verify that $\mathsf{E} = E/N$. On the other hand, using (7), we obtain

$$\left(\frac{\partial E}{\partial N}\right)_{T,V} = -\chi_0 + \epsilon^* + \frac{\pi^2}{12}\frac{k^2T^2}{\epsilon^*} \neq \frac{E}{N}. \tag{1106, 15}$$

It follows from (15) that the temperature coefficients of $(\partial E/\partial N)_{T,V}$ and of $E/N$ are also not equal.

**§ 1107. Adaptation of formulae to metals.** In the preceding section we have obtained a set of mutually consistent thermodynamic formulae for an electron gas in an enclosure of uniform potential energy $-\chi_0$, with $-\chi_0$ treated as independent of $T$ and of $N/V$. When we come to apply this model to the free electrons of a metal, we must be careful not to stretch the model beyond breaking-point. When we insert numerical values we find that $P_e$ in a metal at ordinary temperatures is about a million atmospheres, so that there is no sense in regarding $P_e$ as the contribution of the electrons to the real pressure $P$. The paradox is due to our having assumed $\chi_0$ independent of $V$. Actually $P_e$ is merely the kinetic contribution of the electrons to $P$ and this will be balanced by an opposite almost equal term $N(\partial\chi_0/\partial V)_N$ which has hitherto been assumed zero. It is therefore evident that the model is completely inadequate for explaining any phenomena connected with pressure or volume change.

We can, however, obtain a set of completely consistent formulae by modifying the formulae of § 1106 to take account of a dependence of $\chi_0$ on $V$ or $V/N$. We retain formula (1106, 8) for the free energy. Since $\chi_0$, in any case, represents a rather crude average potential energy of a free electron

obtained by smoothing the attractions of the atomic ions, we may regard formula (1106, 8) as defining $\chi_0$ for given $T$ and given $V$. The essential assumption which we now make is that $\chi_0$ depends only on $V$, and that when $T$ is varied the change in $\chi_0$ is determined entirely by the change in $V$. We accordingly write (1106, 8) in the more precise form

$$F_e = N\{-\chi_0(V)+\tfrac{3}{5}\epsilon^*(V)-\tfrac{1}{4}\pi^2k^2T^2/\epsilon^*(V)\}. \qquad (1107,1)$$

We can now derive all the equilibrium properties by pure thermodynamics. In particular we obtain

$$E_e = -T^2\,\partial(F_e/T)/\partial T = N\{-\chi_0(V)+\tfrac{3}{5}\epsilon^*(V)+\tfrac{1}{4}\pi^2k^2T^2/\epsilon^*(V)\}, \quad (1107,2)$$

of the same form as (1106, 9). For the pressure $P_e$ we obtain, however, instead of (1106, 10)

$$P_e V = V\frac{\partial\chi_0}{\partial V}+\tfrac{2}{5}\epsilon^*+\tfrac{1}{6}\pi^2\frac{k^2T^2}{\epsilon^*}. \qquad (1107,3)$$

This $P_e$ is now the genuine total contribution of the free electrons to the total pressure exerted on or by the metal. It must represent the difference in the total pressure exerted under otherwise similar conditions by an assembly containing free electrons and an assembly without them. We may conclude that $P_e$ can be at most of the same order as the actual pressure $P$. We may regard (3) as determining $P_e$ for given $V$, or alternatively as determining $V$ for given $P_e$. In particular at ordinary low pressures we may use the approximation

$$V\frac{\partial\chi_0}{\partial V}+\tfrac{2}{5}\epsilon^*+\tfrac{1}{6}\pi^2\frac{k^2T^2}{\epsilon^*} = 0, \qquad (1107,4)$$

and regard this equation as determining $V$. For the partial potential $\mu_e$ of an electron we derive from (1)

$$\mu_e = \left(\frac{\partial F_e}{\partial N}\right)_V = \left(\frac{\partial F_e}{\partial N}\right)_v - \frac{V}{N^2}\left(\frac{\partial F_e}{\partial V}\right)_N$$

$$= -\chi_0+V\frac{\partial\chi_0}{\partial V}+\epsilon^*-\frac{\pi^2}{12}\frac{k^2T^2}{\epsilon^*}. \qquad (1107,5)$$

We can verify that formulae (1), (3) and (5) are consistent with the necessary equalities

$$G_e = F_e+P_eV = N\mu_e. \qquad (1107,6)$$

Substituting from (4) into (5) we obtain for ordinary low pressures the alternative form for $\mu_e$,

$$\mu_e = -\chi_0+\tfrac{3}{5}\epsilon^*-\tfrac{1}{4}\pi^2\frac{k^2T^2}{\epsilon^*}. \qquad (1107,7)$$

Alternatively we could obtain (5) directly from (1) by noticing that at ordinary low pressures we have

$$\mu_e = F_e+PV_e \simeq F_e = F_e/N. \qquad (1107,8)$$

We shall denote by $\chi$ the average energy required to take a single electron at constant $T$, $V$ from the interior of the metal to rest outside the metal, leaving behind an equilibrium distribution. With this definition of $\chi$, the thermodynamic energy of evaporation is $\chi+\frac{3}{2}kT$. Using (2) we have

$$\chi = -\left(\frac{\partial E_e}{\partial N}\right)_{T,V} = -\left(\frac{\partial E_e}{\partial N}\right)_{T,v} + \frac{V}{N^2}\left(\frac{\partial E_e}{\partial V}\right)_{T,N}$$

$$= \chi_0 - V\frac{\partial \chi_0}{\partial V} - \epsilon^* - \frac{\pi^2}{12}\frac{k^2T^2}{\epsilon^*}. \qquad (1107, 9)$$

Using (4) we can rewrite (9) in the alternative form

$$\chi = \chi_0 - \tfrac{3}{5}\epsilon^* + \frac{\pi^2}{12}\frac{k^2T^2}{\epsilon^*}. \qquad (1107, 10)$$

One further quantity which we shall require is the work $\eta_0$ needed to take a single electron from rest inside the metal to rest outside the metal. This work is not merely $\chi_0$, because the removal of a single electron changes $N/V$, and so the value of $\chi_0$ for the remaining electrons. This process of course does not leave behind an equilibrium distribution, since it leaves the lowest state empty. According to the approximations of the present discussion $\eta_0$ is given by

$$\eta_0 = \chi_0 + N\left(\frac{\partial \chi_0}{\partial N}\right)_V = \chi_0 - V\frac{\partial \chi_0}{\partial V}. \qquad (1107, 11)$$

Substituting from (11) into (5) and into (9), we derive

$$\eta_0 = -\mu_e + \epsilon^* - \frac{\pi^2}{12}\frac{k^2T^2}{\epsilon^*} = \chi + \epsilon^* + \frac{\pi^2}{12}\frac{k^2T^2}{\epsilon^*}. \qquad (1107, 12)$$

In almost all applications the terms in $T^2$ are negligible, and formulae (11) and (12) reduce to

$$\mu_e = -\chi = -\eta_0 + \epsilon^* = -\left(\chi_0 - V\frac{\partial \chi_0}{\partial V}\right) + \epsilon^*. \qquad (1107, 13)$$

**§ 1108. Metals and insulators.** In Sommerfeld's treatment of metals, which we have presented in the foregoing sections, any periodic structure inside the metal is entirely ignored; except for the potential barrier at the surface the electrons are treated as entirely free. This model must be modified to obtain an acceptable electronic theory of matter, for the model must at least provide naturally a means of discriminating between conductors and insulators – that is to say we must be able to specify what electrons are more or less "free" and therefore able to conduct, and what electrons are "bound" and cannot. This discrimination becomes possible when the periodic variations of potential inside the crystal (metal or insulator) are taken into account.

Considerable progress has been made in recent years in the more accurate treatment of electrons in metals and insulators.* It would require too much space to give an adequate account of this work and we shall not attempt to do so here. It is, however, of such importance that we consider it advisable to include a purely qualitative description of the theory.

The motion of an electron in a triply periodic field of force can be studied by either of two methods of approximation, but Schrödinger's equation cannot be solved exactly except for the one-dimensional case. We may start with the atoms of the crystal in correct array but at large separations, use atomic eigen functions for the first approximation to the electronic states, and enquire how the atomic states are perturbed when the separation is decreased to the separation of the actual crystal. Alternatively we may start with the electrons moving freely in an enclosure of uniform potential and then examine how the electronic states are modified by small periodic variations in the potential, with a period equal to the lattice constant of the crystal. Both methods lead to the same general results, and one or other may give the better detailed picture according to circumstances—the atomic starting-point for the most tightly bound states, and the uniform potential starting-point for those least tightly bound.

For our immediate purpose of describing the general nature and distribution of electronic states in a crystal the atomic starting-point will prove satisfactory. Consider first a set of $N$ similar nuclei in a regular crystalline array expanded to large separations. For each set of values of the three quantum numbers (spin excluded) each nucleus provides one state for each of the two directions of electron spin; thus the $N$ nuclei provide $2N$ similar states. At large separations these have all the same energy and form in fact one $2N$-fold degenerate state. If now the scale of the nuclear array is reduced, this $2N$-fold degenerate state is split by the interactions of the other nuclei into a group of states distributed in energy over a band of energies, whose width increases as the scale of the array diminishes, but remains independent of $N$ at least when $N$ is large. In general the band will contain $N$ distinct energy levels in each of which the electron can have either spin. Such a band can accommodate just $2N$ electrons and no more. The energies of its states will be modified by the electronic charges as the later electrons are added, but, as always, these charges cannot modify the number and general properties of the states. Since the breadth $B$ of the band is independent of $N$, the order of the separation between states of neighbouring energy will be $B/N$; this is very small when $N$ is large, and for a

* There is now a great choice of literature to which the reader may refer for a more detailed general account of this field: in particular Brillouin, *Die Quantenstatistik* (1931); Sommerfeld and Bethe, *Handb. d. Physik*, Ed. 2, *Elektronentheorie der Metalle*, **24**, pt. 2, 333 (1933); Mott and Jones, *Properties of Metals and Alloys* (Oxford, 1936).

substantial crystal the set of states in the band forms practically a continuum. It can be shown that each atomic eigen function, corresponding to a definite electron energy, is converted by the interaction in the crystal into a band of $N$ states each capable of accommodating two electrons of opposite spin. These energy bands belonging to different atomic eigen functions may or may not overlap; whether they do or not may make an essential difference in the electronic properties of the lattice.

At the absolute zero of temperature the electrons of the lattice will occupy the necessary number of states of lowest energy available. Even at high temperatures this remains approximately true. The lowest bands will all be completely full and the electrons in these bands may be called *bound electrons*. If the highest band or bands containing electrons are not completely full, these electrons may be called *free electrons*. The free electrons will fill the lowest states (exactly at the absolute zero and approximately at finite temperatures) immediately above the bands already filled with the bound electrons. These states may all lie in one band, as in the case of the alkali metals, or they may lie in two overlapping bands, as in the case of the transition metals. We shall discuss these examples in the next section. The electrical properties of the crystal will now be entirely different according as the highest band containing electrons at the absolute zero is partly or completely full, that is to say according as there are or are not any free electrons.

We may now make a start by describing the very different properties of good and bad solid conductors of electricity, which show that a classification into good and bad is no mere trivial one. Good conductors (metals) have an electrical resistance which always rises with the temperature and with the presence of increasing amounts of impurities. Bad conductors have a resistance which falls rapidly as the temperature rises (until the temperature passes a definite limit) and generally falls as the impurity content rises. Bad conductors with these properties are called semi-conductors, or insulators when very bad. There is no such sharp line of demarcation between semi-conductors and insulators, as there is in general between these substances and metals.

The quantum theory of electrons in a periodic field provides a theoretical basis for this classification. If the highest band of allowed states, containing any electrons at low temperatures, is only partly full of electrons, then at all temperatures there are electrons available at the top of the full levels, in number nearly independent of the temperature, which are free to make transitions to neighbouring empty states, and the substance is a good conductor, a metal. If on the other hand the highest band containing any electrons at low temperatures is exactly full of electrons, and separated from

the next higher band by a distinct gap of disallowed energies, there are no electrons at low temperatures free to make any transitions, and the substance is an insulator. At higher temperatures the electrons will not be all in the highest normally occupied band, but a few will be thermally excited to the higher empty band. The general result must be that there will at higher temperatures be an increasing number of free electrons in the almost empty band, and therefore also of free holes which function as free positive electrons in the almost full band, both of which can make transitions to neighbouring states, and so the substance will conduct more and more freely as the temperature rises. Without going into any details it is already clear that we have the necessary basis for distinction between metals and insulators.

It is at present not possible to carry through the actual calculations necessary to decide in all cases whether a set of $N$ atoms (or molecules) of a given type, when they combine to form a crystal lattice, will form a metal or an insulator. We shall merely describe what does in fact happen in a few special cases. An alkali atom has a single valency electron in an $s$ state, well separated in energy from the states of the other core electrons. In the crystal formed from $N$ atoms there is an $s$ band capable of accommodating $2N$ electrons, and there are only $N$ electrons present to go into it. The solid alkalis are therefore metals. We might go further and try to argue that any atom of odd valency (or molecule of odd residual valency such as NO or TiN) must also form a metal in the solid state. This, however, is not always correct, as can be seen most clearly by considering the halogens. A halogen atom has an incomplete outer shell containing seven valency electrons instead of eight. If the atoms could form an atomic lattice, the four atomic eigen functions of the outer shell would form a band or bands of states capable of holding $8N$ electrons; only $7N$ would be present and a metal would result. But in fact this is not what occurs: the halogen atoms from energy considerations prefer first to form molecules of two atoms rather than crystal lattices, and the lattices are built up from these molecules, not from atoms. The molecular electronic states are all fully occupied by two electrons each, and can form bands of crystal states which are all completely full (or completely empty) so that the solid is an insulator. In the same way, while TiN forms a typical metal, NO does not. Presumably the molecules first polymerize to $N_2O_2$, in which all the molecular electronic states are fully occupied, and give rise to fully occupied lattice bands. The converse can also happen. Atoms with electronic states all full in the free state need not necessarily give rise to insulators, for if there are other atomic states not far removed in energy from the ground state, the corresponding bands may overlap and the lattice have the properties of a metal. The alkaline earth

metals provide an example. The free atom has two *s* electrons filling the last *s* group, but in the crystal the *s* and *p* bands overlap and the crystal is a metal. It is at present therefore still necessary to discuss the electrical properties of each crystalline solid on the basis of explicit assumptions as to the nature and arrangement of the electronic bands, the assumptions being chosen in each case to accord with the known properties of the substance, whether those of a metal or those of an insulator. The theory provides a natural place for both types of substance.

**§ 1109. Energy bands in actual metals.** We described in the preceding section how the complete set of crystalline electronic states is composed of a series of bands which may or may not overlap. It will be convenient to use the expression group of bands to refer to several bands that mutually overlap, but which do not overlap the bands in other groups. The properties of a metal, which depend on the electrons, will be determined by the distribution of energy levels in a band and by the extent to which several bands form groups of overlapping bands. The structure and relative positions of the partly filled bands, that is to say the bands containing the free electrons, are particularly important.

It is convenient to describe the distribution of electronic energy states by a function $g(\epsilon)$, such that in a metal of volume $V$ the number of states with energy in the range $\epsilon$, $\epsilon+d\epsilon$ is equal to

$$Vg(\epsilon)\,d\epsilon, \qquad (1109,1)$$

each such state being capable of accommodating two electrons, one with each direction of spin. Some values of the energy will be confined to a single band, others to two overlapping bands. In an energy range where two bands 1 and 2 overlap, $g(\epsilon)$ will be of the form

$$g(\epsilon) = g_1(\epsilon)+g_2(\epsilon), \qquad (1109,2)$$

where $g_1(\epsilon)$, $g_2(\epsilon)$ are the distribution functions for the states in the two overlapping bands. The form of $g(\epsilon)$, or of $g_1(\epsilon)$ and $g_2(\epsilon)$, will depend not only on the nature of the atoms of which the metal consists but also on their arrangement in the crystal. The two most important structures are the face-centred cubic and the body-centred cubic. The determination of $g(\epsilon)$ for a metal of atoms of a given kind with a given crystalline structure is a problem in quantum theory, which like so many other problems is soluble in principle but extremely complicated in practice. In spite of its difficulty considerable progress has been made* in the theoretical calculation of $g(\epsilon)$ for certain metals with cubic lattices, and these calculations, so far as they go, have been corroborated by experimental data on the absorption of ultra

* See for example Mott and Jones, *Properties of Metals and Alloys* (Oxford, 1936).

soft X-rays. We can here only describe extremely briefly a few of the most important results of such calculations.

We shall first describe the general form of $g(\epsilon)$ for a single band. At the bottom of the band $g(\epsilon)$ is of the form

$$g(\epsilon) \propto (\epsilon+\eta_b)^{\frac{1}{2}}, \tag{1109, 3}$$

where $-\eta_b$ is the energy at the bottom of the band. At the top of the band $g(\epsilon)$ has the form

$$g(\epsilon) \propto (-\eta_t-\epsilon)^{\frac{1}{2}}, \tag{1109, 4}$$

where $-\eta_t$ denotes the energy at the top of the band. When $g(\epsilon)$ is plotted against $\epsilon+\eta_b$ the curve obtained begins with the form (3), then rises above the curve (3); there will somewhere be a discontinuity of slope, and the curve will fall and cut the curve (3). There may be other sudden breaks, determined by the crystal structure, before the curve finally ends with the form (4).

When several bands overlap, the resultant $g(\epsilon)$ for the group is constructed from those of the constituent bands according to formula (2). As a simple illustration we show in Fig. 3 the approximate form of $g(\epsilon)$ according to Jones and Mott* for the first two overlapping bands formed from the $s$ and $p$ states of atoms in a crystal with body-centred cubic structure. The curve $OABCE$ represents the lower band; the curve $FDG$ the beginning of the upper band; the curve $OABCDG$ the resultant $g(\epsilon)$ for the pair of bands. The curve $OBG$ is a parabola corresponding to formula (3). Fig. 4 is a similar diagram due to Slater† for the overlapping bands formed from the $3d$ and $4s$ atomic states in nickel. We shall discuss this figure further in the next section.

It should be observed that on Sommerfeld's theory we have, by (1102, 7),

$$g(\epsilon) = 2\pi\left(\frac{2m_e}{h^2}\right)^{\frac{3}{2}}(\epsilon+\eta_0)^{\frac{1}{2}}, \tag{1109, 5}$$

and this may be regarded as a special case of (3), if we identify $\eta_0$ with $\eta_b$. In general the numerical coefficient of $(\epsilon+\eta_b)^{\frac{1}{2}}$ will be greater, and sometimes considerably greater, than the coefficient of $(\epsilon+\eta_0)^{\frac{1}{2}}$ in (5). In the case of the alkali metals, for special reasons the coefficient will be approximately given by formula (5). Moreover, these metals have only one free electron per atom and so the $s$ band containing these electrons will be just half full. The highest energy level that is full will be approximately at $A$ in Fig. 3.

In the next section we shall discuss briefly the bearing of $g(\epsilon)$ on the heat capacities of metals. For discussing the thermionic properties of metals it is not necessary to know the form of $g(\epsilon)$. It is sufficient to use the approximation, which is accurate at the absolute zero, that all the $N$ elec-

* Jones and Mott, *Proc. Roy. Soc.* A, **162**, 49 (1937). † Slater, *Phys. Rev.* **49**, 537 (1936).

trons occupy the $\frac{1}{2}N$ lowest states, two in each state. If the work required to remove an electron from the highest occupied state and take it to rest in the gas is denoted by $\chi$, we may continue to use the formulae

$$\mu = -\chi, \tag{1109, 6}$$

$$\lambda = e^{-\chi/kT}, \tag{1109, 7}$$

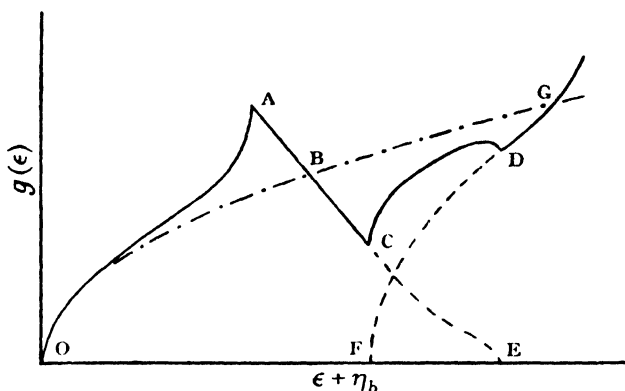



Fig. 3. Distribution of energy levels in bands formed from atomic *s* and *p* states. —·—·—·— for free electrons; -------- individual bands; ——— total $g(\epsilon)$.

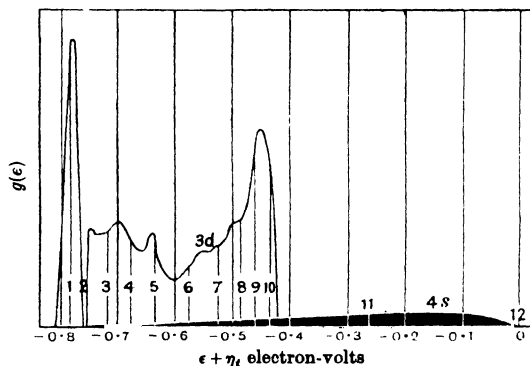



Fig. 4. Distribution of energy levels for copper and approximately for nickel. The 3*d* and 4*s* bands are shown separately. Vertical lines indicate the portion of the bands filled by 1, 2, ..., 12 electrons per atom respectively.

already derived in § 1107 for Sommerfeld's model. To establish (6) or (7) we have merely to observe that, whatever the form of $g(\epsilon)$, we have for a partly filled group of bands containing $N$ (free) electrons

$$N = V\int_{-\eta_b}^{-\eta_t} \frac{2g(\epsilon)\,d\epsilon}{e^{(\epsilon-\mu)/kT}+1}, \tag{1109, 8}$$

where $-\eta_b$, $-\eta_t$ denote the energy levels of the bottom and top of the band respectively. We now use the same approximation as in § 1103, namely

$$\left.\begin{array}{ll} e^{(\epsilon-\mu)/kT} \simeq 0 & (\epsilon < \mu) \\ e^{-(\epsilon-\mu)/kT} \simeq 0 & (\epsilon > \mu) \end{array}\right\}. \tag{1109, 9}$$

Formula (8) now reduces to

$$N = V\int_{-\eta_b}^{\mu} 2g(\epsilon)\,d\epsilon. \tag{1109, 10}$$

But, if we denote by $-\chi$ the energy of the highest states that are completely filled at the absolute zero, we have

$$N = V\int_{-\eta_b}^{\chi} 2g(\epsilon)\,d\epsilon. \tag{1109, 11}$$

Comparing (10) with (11) we deduce (6). To the same approximation the electronic free energy and the energy are given by

$$F_e = E_e = +V\int_{-\eta_b}^{-\chi} 2g(\epsilon)\,\epsilon\,d\epsilon = -N\eta_b + V\int_{\eta_b}^{-\chi} 2g(\epsilon)\,(\epsilon+\eta_b)\,d\epsilon. \tag{1109, 12}$$

If we vary $N$ in (12) and (11) and divide the one by the other, we obtain

$$(\partial F/\partial N)_V = -\chi. \tag{1109, 13}$$

One can also obtain more accurate formulae corresponding to the degree of approximation of § 1104. We shall not give derivations,* but will quote the results:

$$F_e = -N\eta_b + V\int_{\eta_b}^{\chi} 2g(\epsilon)\,(\epsilon+\eta_b)\,d\epsilon - \tfrac{1}{3}\pi^2k^2T^2Vg(-\chi), \tag{1109, 14}$$

$$E_e = -N\eta_b + V\int_{-\eta_b}^{\chi} 2g(\epsilon)\,(\epsilon+\eta_b)\,d\epsilon + \tfrac{1}{3}\pi^2k^2T^2Vg(-\chi), \tag{1109, 15}$$

$$S_e = \tfrac{2}{3}\pi^2k^2Tg(-\chi), \tag{1109, 16}$$

$$\mu_e = -\chi - \tfrac{1}{6}\pi^2\frac{k^2T^2}{g(-\chi)}V\left(\frac{\partial g}{\partial \epsilon}\right)_{\epsilon=-\chi}, \tag{1109, 17}$$

with $\chi$ still defined by (11).

**§ 1110. Electronic contribution to heat capacities.** In Chapter IV we were able to give a generally satisfactory account of the heat capacities of metals and other solids, in which we entirely ignored any contribution that might be made by the free electrons of a metal. We can now verify that such a contribution will in fact usually be negligible except at very low temperatures.

* These are given, for example, by Mott and Jones, *Properties of Metals and Alloys*, pp. 176–179.

We can begin by using Sommerfeld's model. The energy of the electrons is then given by formula (1107, 2), and so the contribution of each free electron to the heat capacity at constant volume will be given by

$$\frac{C_e}{k} = \frac{1}{Nk}\left(\frac{\partial E_e}{\partial T}\right)_{V,N} = \tfrac{1}{2}\pi^2\frac{kT}{\epsilon^*}. \qquad (1110, 1)$$

In §1104 we calculated that for copper $\epsilon^*/k = 8\times 10^4$ deg. so that $C_e/k = 6\times 10^{-5}\,T$, which is negligible at all ordinary temperatures. We are thus free to apply the idea of a gas of free electrons to thermionic, photoelectric, thermoelectric and conductivity problems, without upsetting earlier conclusions based on the theory of crystals.

Actually Sommerfeld's formula (1) is probably applicable only to the alkali metals and then only for special reasons. Generally we must use instead formula (1109, 15) for the energy. We then obtain for the electronic contribution to the atomic heat capacity

$$\frac{C_e}{k} = \frac{1}{Nk}\left(\frac{\partial E_e}{\partial T}\right)_{V,N} = \tfrac{2}{3}\pi^2 kTVg^*, \qquad (1110, 2)$$

where $V$ is the atomic volume, and we have written $g^*$ instead of $g(-\chi)$ for the value of the distribution function $g(\epsilon)$ at the energy $-\chi$ of the highest occupied state at the absolute zero. The absolute value of $C_e$ is thus determined by $Vg^*$. Even without knowing the precise value of $g^*$ we can draw several interesting conclusions from formula (2).

Whatever the value of $g^*$, it follows from (2) that

$$C_e \propto T. \qquad (1110, 3)$$

For the contribution $C^{ac}$ of the acoustical modes to the heat capacity we found in Chapter IV that in the limit of low temperatures

$$C^{ac} \propto T^3. \qquad (1110, 4)$$

Hence, however small $C_e$ may be in absolute value, it will become the dominant term in the heat capacity if the temperature is sufficiently low. When numerical values are inserted it is found that, according to the Sommerfeld model, $C_e$ becomes comparable to $C^{ac}$ in the region of a few degrees K. When $g^*$ is appreciably greater than the value corresponding to Sommerfeld's model, $C_e$ is correspondingly more important. The formula (3) has in fact been confirmed experimentally† by Keesom and Kok for silver and zinc. They measured the heat capacity between 1·7 and 4° K. and found it to be greater than that given by extrapolation of Debye's $T^3$-law. The excess heat capacity could be represented by a relation of the form (3). The proportionality constant for silver is approximately that given by

† For references see Table 1.

Sommerfeld's formula (1), if one assumes one free electron per atom. For zinc the proportionality constant is rather smaller but has not been determined accurately. Similar results have been obtained more recently for copper, the proportionality constant being somewhat greater than for silver.

It thus appears that Sommerfeld's model, crude as it is, is able to give the value of the electronic heat capacities in silver, copper and zinc within a factor of about 2. The model may perhaps apply still better to the alkali metals,† but experimental data for the heat capacities at temperatures around 1° K. are not available. For several metals among the transition elements the relation (3) has also been verified, but the proportionality constants are several times greater than those corresponding to Sommerfeld's model. The proportionality factors for the several metals are collected in Table 1.

TABLE 1

*Heat capacities of metals at temperatures in neighbourhood of* 1° K., *where* $C_e \propto T$

| Metal | $10^4 c_e/kT$ (deg.$^{-1}$) | References |
|---|---|---|
| Ag | 0·8 | Keesom and Kok, *Physica*, **1**, 770 (1934) |
| Cu | 0·9 | Kok and Keesom, *Physica*, **3**, 1035 (1936) |
| Ni | 8·8 | Keesom and Clark, *Physica*, **2**, 513 (1935) |
| Pd | 16 | Pickard, *Nature*, **138**, 123 (1936) |
| Pt | 8·1 | Kok and Keesom, *Physica*, **3**, 1035 (1936) |
| Fe | 6·0 | Duyckaerts, *Physica*, **6**, 401 (1939) |

We shall not discuss these values in detail.‡ The most important point is that a high coefficient must mean a high value of $g^*$. The reason why $g^*$ has a relatively high value for a transition metal can be made clear by a comparison of nickel and copper. The electron bands shown in Fig. 4 are constructed from the 3*d* states and the 4*s* states of free Cu atoms. It is convenient to refer to the lower band as the 3*d* band and to the higher band as the 4*s* band, though this is not an accurate description of the nature of the bands. In nickel the form of $g(\epsilon)$ will not be exactly the same as in copper, but the general shape will be similar and we can use the same diagram to describe the electronic distribution in nickel. In copper the highest occupied level is at the place marked 11, and so in a crystal of copper containing $N$ atoms there are $10N$ electrons in the 3*d* band and $N$ in the 4*s* band. In

† See, in particular, Slater, *Phys. Rev.* **45**, 794 (1934).

‡ For such a discussion see *S.M.* p. 391, or Mott and Jones, *Properties of Metals and Alloys*, p. 192. An instructive elementary review of this field has been given by Sommerfeld, *Ann. d. Phys.* **28**, 1 (1937).

nickel, on the other hand, the highest occupied level is at the place marked 10, and so in a crystal of $N$ atoms there are about $9{\cdot}4N$ electrons in the $3d$ band and about $0{\cdot}6N$ electrons in the $4s$ band. It is now immediately evident from the diagram that $g^*$, and consequently $C_e$, is much greater for nickel than for copper. For similar reasons the values of $g^*$ for palladium, platinum and iron will be high as compared to copper, zinc and silver.

**§ 1111. Elementary theory of an electron atmosphere.** Let us now consider an assembly consisting of the metal and the vapour phase. Since the evaporated electron density will prove to be very small, its space charge can, as a first approximation, be neglected, and the number of electrons in the metal can be assumed to be normal; actually any deficiency of electrons in the metal would always be replaced by conduction.

In the vapour phase (denoted by the superscript $G$) the electron density is so low that the classical formula (1101, 7) is applicable. We have therefore for the absolute activity of electrons in the vapour

$$\lambda_e^G = \nu^G \frac{h^3}{2(2\pi m_e kT)^{\frac{3}{2}}}, \qquad (1111, 1)$$

where $\nu^G$ $(=N^G/V^G)$ denotes the number of electrons in unit volume in the vapour phase. For the electrons in the metal, we have with sufficient accuracy according to (1107, 13)

$$\mu_e^M = -\chi = -\eta_0 + \epsilon^*, \qquad (1111, 2)$$

where the superscript $M$ refers to the metal. The absolute activity of the electrons in the metal is therefore

$$\lambda_e^M = e^{-\chi/kT}. \qquad (1111, 3)$$

As we saw in § 1109, formula (3) is independent of the distribution of energy states provided $\chi$ is correctly defined.

The condition for equilibrium between vapour and metal is

$$\lambda_e^G = \lambda_e^M. \qquad (1111, 4)$$

Substituting from (1) and (3) into (4), we obtain

$$\nu^G = \frac{2(2\pi m_e kT)^{\frac{3}{2}}}{h^3} e^{-\chi/kT}. \qquad (1111, 5)$$

Apart from the factor 2 for electron spin, formulae substantially equivalent to (5) had been obtained before the development of modern quantum theory.†

† The earliest derivation appears to be due to v. Laue, *Ann. d. Phys.* **58**, 695 (1919). For other early references see O. W. Richardson, *The Emission of Electricity from Hot Bodies*, Ed. 2 (Longmans, 1921); Schottky, *Zeit. Phys.* **34**, 645 (1925).

**§ 1112. Vapour pressure constant of electrons.** It is worth noticing that by applying the perfect gas equation to the electrons in the vapour, we can transform (1111, 5) to

$$\log p_e = -\frac{\chi}{kT} + \tfrac{5}{2}\log T + \log\left\{\frac{2(2\pi m_e)^{\frac{3}{2}} k^{\frac{5}{2}}}{h^3}\right\}, \qquad (1112, 1)$$

where $p_e$ denotes the vapour pressure of the electrons in equilibrium with the metal. Thus the vapour pressure constant of the electron is

$$i_e = \log\left\{\frac{2(2\pi m_e)^{\frac{3}{2}} k^{\frac{5}{2}}}{h^3}\right\}, \qquad (1112, 2)$$

which is the normal value for a particle of mass $m_e$ with two possible orientations. This formula, apart from the factor 2 for electron spin, was obtained by Dushman.*

**§ 1113. Thermionic emission.** The phenomena of the emission of electricity from hot bodies are well known.† We cannot here describe experimental details. It is sufficient to record that an incandescent metal emits electrons and to a less extent positive ions at a rate which is extremely sensitive to the temperature. The phenomena actually observed depend in general on these rates of emission, for the system studied experimentally is usually not in an equilibrium state. But since there must be an equilibrium state for the corresponding isolated system, we are led by these phenomena to believe that when equilibrium is set up between a metal and its surroundings (gas or vacuum), the metal is in equilibrium with a vapour of electrons and perhaps of positive ions as well. If we have chosen a suitable model, this equilibrium so far as it concerns electrons should be adequately described by the formulae of the preceding sections.

It has not proved possible to observe the electron density given by (1111, 5) or the corresponding electron vapour pressure. The quantity observed is always a current—the maximum current that can be drawn from an incandescent wire by an external voltage large enough to sweep away the electrons as fast as they are emitted, but not large enough to produce a sensible potential gradient near the emitting surface. Such a saturation current measures the rate of emission of electrons by the hot solid. About such rates of emission neither thermodynamics nor the equilibrium theory of statistical mechanics have anything to say. We must appeal to some mechanism, which however, and here the equilibrium theory comes in,

* Dushman, *Phys. Rev.* **21**, 625 (1923).

† For a general account see O. W. Richardson, *The Emission of Electricity from Hot Bodies*, Ed. 2 (Longmans, 1921); K. T. Compton and Langmuir, *Reviews of Mod. Physics*, **2**, 123 (1930). A more recent account is Reimann, *Thermionic Emission* (Chapman and Hall, 1934) from which we have taken the greater part of the numerical data.

must be consistent with the equilibrium state when allowed to act in a normal manner. It must be true, for example, that the rates of emission and return of electrons are equal in the equilibrium state. We now assume that, when the external voltage is applied and the saturation current measured, the rate of emission of electrons is unaltered. Since this rate is determined by the internal state of a conductor, and the voltages in question are not large, this assumption may be accepted.

**§ 1114. Rate of evaporation of electrons.** Now that we possess an adequate picture of the electronic state inside a metal, it is possible to calculate directly the rate of emission of electrons under equilibrium conditions. It is possible, however, to arrive formally at the same result indirectly and more simply by calculating the rate of return of electrons to the metal and we give this calculation first on account of its historical importance.

The electrons in the vapour have the usual Maxwellian distribution in velocity and position, and therefore, by (334, 2), the total number of electrons striking unit area in unit time is

$$\nu^G\left(\frac{kT}{2\pi m_e}\right)^{\frac{1}{2}}. \qquad (1114, 1)$$

Substituting from (1111, 5) into (1), we obtain for the number of gaseous electrons striking unit area of the metal surface per unit time in the equilibrium state

$$\frac{4\pi m_e k^2 T^2}{h^3} e^{-\chi/kT}. \qquad (1114, 2)$$

If a fraction $r$ of these is reflected again, the number of electrons condensing per unit area of the metal per unit time is

$$(1-r)\frac{4\pi m_e k^2 T^2}{h^3} e^{-\chi/kT}. \qquad (1114, 3)$$

In the equilibrium state the rates of evaporation and of condensation must be equal. Hence (3) gives also the rate of evaporation of electrons per unit area per unit time in the equilibrium state.

We have given the simplest and oldest derivation of (3) for the rate of evaporation, but it is of interest to confirm (3) by a direct derivation. Only those electrons can get out whose kinetic energy $\zeta$ perpendicular to the surface exceeds the energy $\eta_0$ defined at the end of § 1107. It is assumed that the motion normal to the surface is unaffected by the other velocity components, which is correct when the atomic variations of the potential are neglected. If $n(\zeta)\,d\zeta$ is the number of electrons incident on unit area of surface from the inside per unit time with normal kinetic energy in the range

$d\zeta$ and $D(\zeta)$ is the chance that such an electron will emerge, then the number of electrons emerging from unit area per unit time is

$$\int_{\eta_0}^{\infty} n(\zeta)\,D(\zeta)\,d\zeta, \tag{1114, 4}$$

or

$$\bar{D}\int_{\eta_0}^{\infty} n(\zeta)\,d\zeta, \tag{1114, 5}$$

where $\bar{D}$ is a mean transmission coefficient. But it is a well-known quantal theorem that transmission coefficients over any barrier are necessarily the same in both directions† for electrons of each energy group. Hence $\bar{D}$ must be the same as $(1-r)$, and (5) becomes

$$(1-r)\int_{\eta_0}^{\infty} n(\zeta)\,d\zeta. \tag{1114, 6}$$

Substituting for $n(\zeta)$ from (1105, 11), we obtain

$$(1-r)\int_{\eta_0}^{\infty} \frac{4\pi m_e kT}{h^3}\, e^{-(\zeta-\epsilon^*)/kT}\,d\zeta \tag{1114, 7}$$

Performing the integration, we obtain

$$(1-r)\frac{4\pi m_e k^2T^2}{h^3}\, e^{-(\eta_0-\epsilon^*)/kT} \tag{1114, 8}$$

and using (1111, 2) we recover (3).

It follows that the saturation current $-I$ flowing from unit area of the hot body to the collecting electrode is given in electrostatic units by the formula

$$I = (1-r)\frac{4\pi m_e k^2|e|}{h^3}\, T^2 e^{-\chi/kT}, \tag{1114, 9}$$

where $-|e|$ denotes the electronic charge. This is the correct form of Richardson's emission formula. The energy $\chi$ is called the *thermionic work function*. The earliest version of this formula omitted the weight factor 2 for the electron spin, and also the reflection coefficient $r$.

**§ 1115. Transmission coefficient.** To make use of (1114, 9) we require information about the transmission coefficient $(1-r)$. To obtain an accurate theoretical value for $r$ we should require to know the exact form of the potential barrier separating the interior of the metal from the vapour. By assuming approximate forms for the potential barrier one can calculate approximate values for $r$. We shall not give these calculations here. It is sufficient to state that reasonably probable forms for the barrier for a clean metal surface lead to values of $r$ much less than 1, so that $1-r \simeq 1$.

† For example see R. H. Fowler, *Proc. Camb. Phil. Soc.* **25**, 193 (1929).

The transmission coefficient $D(\zeta)$ is a function of $\zeta$ and the shape of the potential barrier and is, of course, independent of the temperature. $\bar{D}$ or $(1-r)$, being an average for all $\zeta \geqslant \eta_0$, is strictly a function of temperature, but actually is almost independent of temperature and of magnitude comparable with unity.*

**§ 1116. Comparison of theory and experiment for clean metals.** We can write the theoretical formula (1114, 9) in the form

$$I = (1-r)AT^2 e^{-\chi/kT}, \qquad (1116, 1)$$

where $A = 120$ amp./cm.² deg.² We may expect that $(1-r)$ is not greatly different from 1. When (1) is compared with the best experiments on carefully cleaned tungsten, regarding $(1-r)$ and $\chi$ as adjustable constants, an excellent fit is obtained with a value of $(1-r)$ about $\frac{1}{2}$. Owing, however, to the dominance of the exponential factor. the observations are not capable of fixing $A$ with a high accuracy. It is therefore probable, if not absolutely certain, that there is a real discrepancy of a factor 2 between the simple theory and experiment. Within a factor of 2 or 3 there is agreement between theory and experiment, not only for tungsten but for several other metals, provided they have been properly cleaned. If, however, the surface of the metal is coated with impurity, quite different values are obtained for $(1-r)A$. The theory has been extended to cover the behaviour of a metal covered with a film, but we shall not discuss this extension. The comparison between (1) and the experimental observations of Davisson and Germer on clean tungsten, recomputed by Dushman,† are shown in Fig. 5, where $\log_{10} I/T^2$ is plotted against $1/T$. The straight line drawn has a slope corresponding to $(1-r)A = 60$ amp./cm.² deg.², or to $1-r = \frac{1}{2}$. The broken line has a slope corresponding to $(1-r)A = 120$ amp./cm.² deg.², or to $r \ll 1$. Later measurements by Dushman and his collaborators‡ completely confirm the measurements of Davisson and Germer.

In Table 2 we give the values of $A$ and $\chi$ considered most reliable by Reimann§ for various metals supposed to be clean. Abnormal values of $(1-r)A$ differing greatly from 120, as in the case of nickel, may be due to films on the metal, but we shall not analyse the data further.||

* For detailed discussion of transmission coefficients, see *S.M.* p. 349.

† Davisson and Germer, *Phys. Rev.* **20**, 300 (1922); Dushman, *Phys. Rev.* **21**, 623 (1923).

‡ Dushman, Rowe, Ewald and Kidner, *Phys. Rev.* **25**, 338 (1925).

§ Reimann, *Thermionic Emission* (Chapman and Hall, 1934), where full references to original sources are given. See also Dushman, *Rev. Mod. Phys.* **2**, 381 (1930).

|| For more detailed discussion see *S.M.* p. 353.

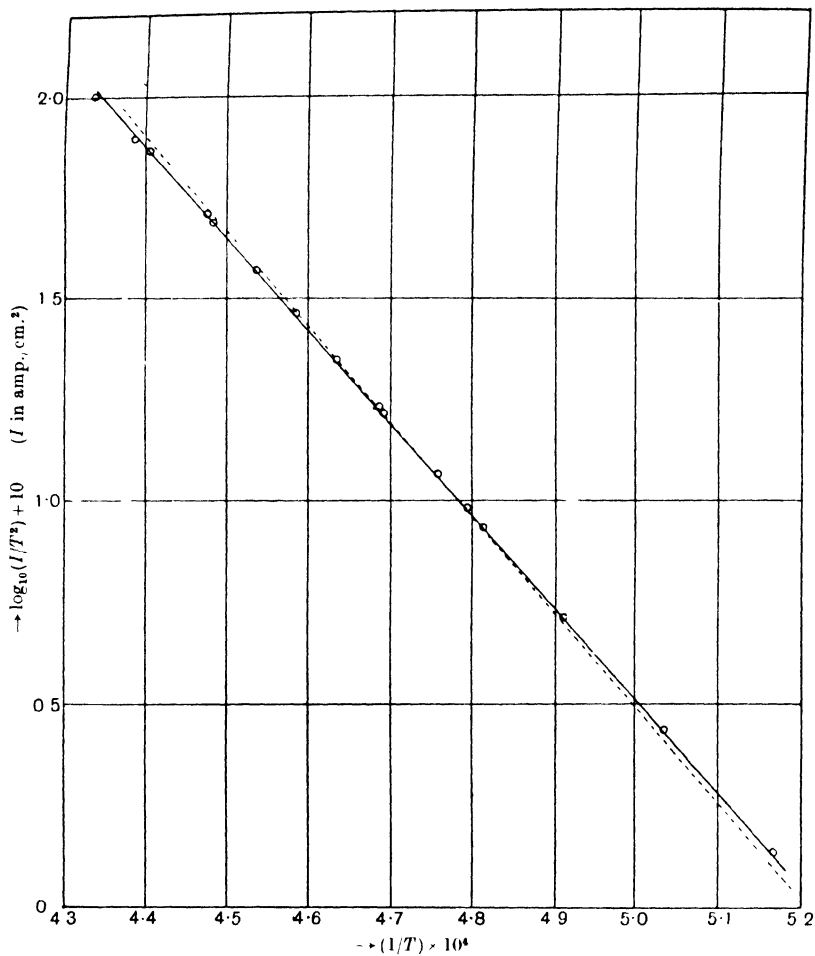



Fig. 5. Thermionic emission current of tungsten. The continuous line corresponds to $r = \frac{1}{2}$, the broken line to $r = 0$.

TABLE 2

*Thermionic emission constants for metals believed clean*

Data as critically selected by Reimann

| Element | $\chi$ electron-volts | $A$ amp./cm.$^2$ deg.$^2$ |
|---|---|---|
| Cs | 1·81 | 162 |
| Ba | 2·11 | 60 |
| Zr | 4·12 | 330 |
| Hf | 3·53 | 14·5 |
| Th | 3·38 | 70 |
| Ta | 4·1 | 60 |
| Mo | 4·15 | 55 |
| W | 4·54 | 60–100 |
| Re | 5·1 | 200 |
| Ni | 5·03 | 1380 |
| Pd | 4·99 | 60 |
| Pt* | 5·40 | 170 |

Where a value of 60 is given for $A$ it usually implies that the observational value is not very different from 60, differing from it perhaps by a factor less than 2, but that the old theoretical value 60 has been *assumed* in the analysis.

* The data for Pt are those of Van Velzer, *Phys. Rev.* **44**, 831 (1933). Previous data are unreliable owing to the metal surface not being clean. All other data in this table are as selected by Reimann.

§ **1117. The photoelectric effect.** When light falls on a cold metal surface, electrons are emitted as soon as the frequency $\nu$ of the incident light exceeds a certain threshold frequency $\nu_0$. This is known as the photoelectric effect. The model of a metal here in use accounts at once for the main features of this emission. For when $T \to 0$, there are no electrons in the metal with a kinetic energy greater than $\epsilon^*$, and plenty with any energy less than $\epsilon^*$. In order that an electron whose initial energy is $\epsilon$ may emerge after absorbing a quantum of energy $h\nu$, it is necessary at the least that

$$h\nu + \epsilon > \eta_0. \quad (1117, 1)$$

The least possible value of $\nu$ satisfying this inequality is

$$h\nu = h\nu_0 = \eta_0 - \epsilon^* = \chi. \quad (1117, 2)$$

The photoelectric threshold frequency $\nu_0$ is thus equal to $\chi/h$. Table 3 compares the observed values of $h\nu_0$ and $\chi$, where both have been satisfactorily determined. The agreement is excellent.

Experiments on the photoelectric effect are not habitually made at low temperatures, and it is necessary to consider the effect of temperature on the number of available electrons for light of given frequency $\nu$. It is at once

evident that there can be no absolutely sharp threshold at temperatures other than zero, and this is borne out by observations now to be discussed.†

TABLE 3

*Comparison for clean metals of experimental values in electron-volts of $h\nu_0$ and of $\chi$*

| Metal | Cs | Ta | Mo | W | Re | Ni | Pd |
|---|---|---|---|---|---|---|---|
| $h\nu_0$ | $\simeq$ 1·9 | 4·11 | 4·15 | 4·54 | 4·98 | 5·01 | 4·97 |
| $\chi$ | 1·81 | 4·12 | 4·15 | 4·54 | 5·1 | 5·03 | 4·99 |

Data from Reimann, where authorities are quoted.

In order that an electron may be emitted, it is necessary that the energy of its motion normal to the emitting surface should exceed $\eta_0$. Its other velocity components are to a first approximation irrelevant. The rate of emission of such electrons must therefore be expected to be proportional to the intensity of the light, the number of suitable electrons striking unit area of the surface in unit time, the chance that they will pick up the quantum $h\nu$ in the proper velocity component, and the chance that they will then be transmitted through the boundary field. When the boundary field is well represented by an image field, as for a clean metal, this last chance hardly varies and may be taken to be unity. With the model here in use, in which the electrons are free inside the metal, the whole excitation takes place in the surface field of the metal. The chance of absorbing the quantum will vary with $\nu$ as in other absorption phenomena, but this variation is not important near $\nu_0$. Thus a good approximation to the photoelectric yield per unit light intensity near the threshold frequency is to take it simply proportional to the number of electrons incident per unit time for which

$$\tfrac{1}{2}p_x^2/m_e + h\nu > \eta_0, \qquad (1117,3)$$

where $p_x$ is the initial momentum of the electron normal to the surface.

Equation (1105, 10) gives the number of such electrons as a function of $p_x$. The photoelectric yield per unit light intensity is therefore proportional to

$$\int_{\{2m_e(\eta_0-h\nu)\}^{\frac{1}{2}}}^{\infty} dp_x \frac{4\pi m_e kT}{h^3} \frac{p_x}{m} \log\{1+e^{(\epsilon^*-p_x^2/2m_e)/kT}\}. \qquad (1117,4)$$

This can be rewritten as

$$\frac{4\pi m_e k^2T^2}{h^3} \int_0^{\infty} dy \log\{1+e^{-y+(h\nu-\chi)/kT}\}. \qquad (1117,5)$$

† This was first established beyond reasonable doubt by the work of Mendenhall's laboratory; see Morris, *Phys. Rev.* **37**, 1263 (1931); Winch, *Phys. Rev.* **37**, 1269 (1931); Cardwell, *Phys. Rev.* **38**, 2041 (1931).

This function should give the photoelectric yield for a clean metal as a function of $\nu$ and $T$ for values of $\nu$ near the threshold $\nu_0 = \chi/h$.

The integral in (5) cannot be evaluated in finite terms but can be computed from simple expansions.* The result can be expressed in the form

$$\log\left(\frac{I}{T^2}\right) = B+\Phi\left(\frac{h\nu-\chi}{kT}\right), \qquad (1117,6)$$

where $\Phi$ is a known function and $B$ is a constant. For each temperature we can then plot observed values of $\log_{10}(I/T^2)$ against $h\nu/kT$, and can plot

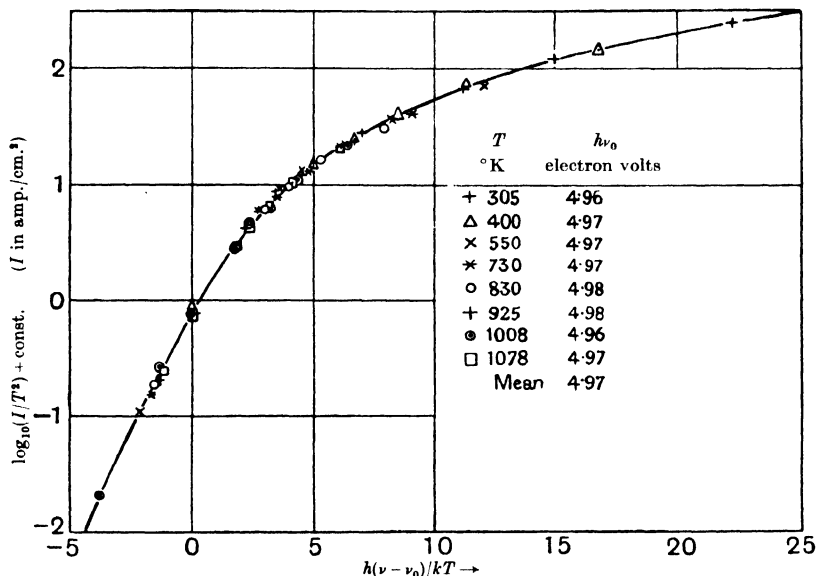



Fig. 6. Analysis of observed photoelectric yields for Pd.

$\Phi(x)$ against $x$ on the same scale. Observations for all temperatures should then be brought to lie on the $\Phi(x)$ curve by suitable shifts of the origins. The shift in the origin of $\nu$ determines accurately the true threshold $\chi = h\nu_0$. An alternative method of analysis has been used by Du Bridge† employing sets of observations for various temperatures and a single frequency. In this method $\Phi(x)$ is plotted against $\log x$ and the observations are similarly treated. The results are in excellent agreement. The calculated function $\Phi(x)$ and the analysis of the observations of Du Bridge and Roehr‡ for palladium are shown in Fig. 6. Some such method as these must always be

* See *S.M.* p. 360. † Du Bridge, *Phys. Rev.* **43**, 727 (1933).

‡ Du Bridge and Roehr, *Phys. Rev.* **39**, 99 (1932).

used in determining the true photoelectric threshold, as empirical extrapolations of the photoelectric yield curve to zero are quite unreliable.† In addition to this analysis of the total photoelectric yield, Du Bridge has shown that the same methods may be used to analyse with almost equal success the normal velocity distribution and the total energy distribution of the photoelectrons emitted by a clean metal as a function of $\nu$ and $T$. The agreement between experiment and theory is all that could be desired.

**§ 1118. Temperature dependence of $\chi$ and of $\chi_0$.** In §1114 when we compared the experimental data with the theory we treated $\chi$ as independent of temperature. Strictly we are not justified in treating $\chi$ as completely independent of temperature. We recall that $\chi$ was defined by (1107, 9), which at ordinary pressures could be replaced by (1107, 10). Since, however, the last terms in both these formulae are, as we have seen, negligible, we may write

$$\chi = \chi_0 - v\frac{\partial \chi_0}{\partial v} - \epsilon^* = \chi_0 - \tfrac{3}{5}\epsilon^*, \qquad (1118, 1)$$

where $v$ denotes the ratio of the volume $V$ of the metal to the number $N_e$ of free electrons in the metal. This formula takes adequate account of the dependence of $\epsilon^*$ on $N_e/V$. Hitherto $\chi_0$ and so $\chi$ have been regarded as completely determined by $v$, that is by $N_e/V$. This is in fact the simplest assumption leading to a reasonable set of self-consistent thermodynamic formulae, but it is an over-simplification. For, according to the model corresponding to this assumption, one would obtain the same change in $\chi_0$ either by removing one electron keeping the volume constant or by a mere expansion of the metal in the ratio $(N_e - 1) : N_e$ and this is certainly not the case. We ought to regard $\chi_0$ as a function of both $N_e/V$ and of $N_n/V$, where $N_n$ denotes the number of atomic nuclei. Since $|N_n - N_e| \ll N_n$ always, it would seem at first sight unnecessary to distinguish between $N_e$ and $N_n$. It is, however, necessary to distinguish between varying $N_e/V$ by evaporation of electrons and varying $N_n/V$ by expansion. Without a much deeper analysis it is not at all clear how our formulae ought to be amended. Incidentally it is not certain, even with our crude model, that the $\chi$ occurring in the formula for the thermionic current is correctly given by (1). It might be argued that as each electron is removed by evaporation, it is replaced by another from the current at the other side of the metal. From this point of view, since $v = V/N_e$ remains unaltered, the excess energy $\chi$ required by the evaporating electron to enable it to escape will be given by

$$\chi = \chi_0 - \epsilon^*, \qquad (1118, 2)$$

† For a general account see Du Bridge, *New Theories of the Photoelectric Effect* (Hermann, 1935).

rather than by (1). In neither case are we entitled to assume that $\chi_0$ is independent of $N_n/V$.

If we tentatively assume that $\chi$ varies slowly with the volume and therefore with the temperature, then over a restricted temperature range we may express such variation in the empirical form

$$\chi = \chi^*(1-aT) \qquad (\chi^*, a \text{ constants}). \qquad (1118, 3)$$

The factor $e^{-\chi/kT}$ in formula (1116, 1) will then become $e^{-\chi^*/kT}e^{a\chi^*/k}$. On comparing formula (1116, 1) with experiment, we should then find an apparent $\chi$ equal to $\chi^*$ and the apparent value of $(1-r)A$ would be increased by the factor $e^{a\chi^*/k}$. For tungsten $\chi^*/k \simeq 5{\cdot}3 \times 10^4$ deg. For the extra factor to be equal to 2 it is sufficient to take

$$a = (\log_e 2)/(5{\cdot}3 \times 10^4) = 1{\cdot}3 \times 10^{-4}\,\text{deg.}^{-1},$$

which is certainly small enough to be permissible.

The *a priori* calculation of $\chi_0$ is prohibitively difficult, and that of its temperature coefficient no easier. We shall briefly discuss the problem, chiefly with the object of explaining its intractability.

We may regard $\chi_0$ as consisting of two parts:

(*a*) the work that would be required if the metallic nuclei in the surface were surrounded by the same symmetrical charge distribution as prevails in the interior, including the work due to the image force;

(*b*) the work due to the electrical double layer in the surface.

These two terms may be referred to loosely as the chemical and electric contributions to $\chi_0$. Any macroscopic experimental measurement of e.g. thermionic current, photoelectric emission, or contact potential, can give information concerning $\chi_0$, but none concerning the two separate terms of $\chi_0$. Such information might be derived only from a detailed theory of the configuration of the electrons and nuclei in the interior and in the surface of the metal. Unfortunately such detailed information is almost entirely lacking.

A refined treatment taking account of the detailed atomic structure inside the metal would allow in principle a computation of the chemical contribution to $\chi_0$, but up to the present only very crude approximations have been obtained.† If such computations could be carried out accurately, it would be possible, by performing them for different values of the lattice constant, to determine the dependence on temperature of the chemical term in $\chi_0$.

A much more difficult problem is the determination of the electrical double layer. An attempt to evaluate its order of magnitude has been made

† See, for example, Wigner and Bardeen, *Phys. Rev.* **48**, 84 (1935).

by Bardeen.* He estimates the double layer at the surface of metallic sodium to be about half an electron-volt. His procedure is to determine approximately the average distribution of electrons assuming the distribution of positive electric charges to be uniform right up to a plane and then drop discontinuously to zero. There is no obvious *a priori* reason for assuming that the spacing of positive nuclei in the surface layer is exactly the same as the spacing in the interior of the metal. It seems more likely that there will be some slight difference of spacing in the surface from that in the interior and that such a difference will vary with the temperature. In that case even the approximate estimation of how the double layer depends on the temperature is prohibitively difficult.

We must reluctantly admit that we are still entirely ignorant of how $\chi_0$ should theoretically depend on the temperature. We may hope that the assumption that $\chi_0$ is independent of temperature is not too bad an approximation. The comparison between the experimental data and the formulae obtained by assuming $\chi_0$ independent of temperature indicates a real discrepancy of the order of a factor 2 in the formula for the thermionic current for tungsten, and this can be accounted for by a temperature coefficient of about $10^{-4}$ deg.$^{-1}$ in $\chi$.

**§ 1119. Volta potentials.** Let us now consider two or more metals in simultaneous equilibrium with a vapour phase. For this purpose we must use a consistent energy zero. We shall use the superscript $Ai$ to refer to the interior of the metal $A$, and the superscript $Ae$ to refer to a point just outside the surface field of the metal $A$. We therefore take as the partial potential† of electrons just outside the metal $A$

$$\mu_e^{Ae} = -kT \log\left\{\frac{2(2\pi m_e kT)^{\frac{3}{2}}}{h^3} \frac{V}{N}\right\} - |e|\,\phi^{Ae}. \qquad (1119, 1)$$

Hitherto it was possible to omit the term $-|e|\,\phi^{Ae}$, because we were not concerned with the distinction between $\phi^{Ae}$ and $\phi^{Be}$, say. Because a metal is a conductor, every energy state of the electrons in the metal $A$ will now be raised by the amount $-|e|\,\phi^{Ae}$ above the value assigned to it when the potential energy of an electron in the vapour phase was assigned the value zero. We must therefore replace formula (1111, 3) by

$$\lambda_e^{Ai} = e^{-(\chi^A + |e|\phi^{Ae})/kT}, \qquad (1119, 2)$$

so that

$$\mu_e^{Ai} = -\chi^A - |e|\,\phi^{Ae}. \qquad (1119, 3)$$

For equilibrium of electrons between the metal $A$ and the vapour we have,

* Bardeen, *Phys. Rev.* **49**, 653 (1936).

† We remind the reader that the partial potentials used throughout this book include all space-dependent potential energies. In this application they are electrochemical potentials.

as usual, equality of $\mu_e^{Ae}$ and $\mu_e^{Ai}$. Using (1) and (3) and denoting the number of electrons per unit volume by $\nu$, we obtain

$$\nu^{Ae} = \frac{2(2\pi m_e kT)^{\frac{3}{2}}}{h^3} e^{-\chi^A/kT}, \qquad (1119, 4)$$

equivalent to (1111, 5).

We shall now obtain the equilibrium condition for electrons just outside the metal $A$ and just outside the metal $B$. We have to equate $\mu_e^{Ae}$, given by (1), with $\mu_e^{Be}$ given by a similar expression. We obtain

$$\frac{\nu^{Ae}}{\nu^{Be}} = e^{|e|(\phi^{Ae}-\phi^{Be})/kT}, \qquad (1119, 5)$$

which is the usual distribution law of Boltzmann for the electrons in the vapour phase.

Finally we can obtain the condition for equilibrium between the electrons in the interiors of metals $A$ and $B$ by equating the expression (3) for $\mu_e^{Ai}$ with a similar expression for $\mu_e^{Bi}$. We obtain

$$\chi^A - \chi^B = -|e|(\phi^{Ae} - \phi^{Be}). \qquad (1119, 6)$$

Even if there is no vapour phase present, but the metals are in contact, equilibrium between their electrons must be maintained, which requires equation (6) to hold. This relation can be verified experimentally since $\chi^A$, $\chi^B$ can be determined for each metal from the photoelectric effect, while the Volta potential difference $(\phi^{Ae} - \phi^{Be})$, being a potential difference between two places in the vapour, can be measured directly. Volta potential differences are difficult to measure, but, when experimental data are available, verification of (6) is satisfactory. The data for two pairs of metals are given as examples in Table 4

TABLE 4

| Metal $A$ | Metal $B$ | $\chi^A$ (electron-volts) | $\chi^B$ (electron-volts) | $\chi^B - \chi^A$ | $\phi^{Ae} - \phi^{Be}$ (volts) | Authority |
|---|---|---|---|---|---|---|
| Ni | Fe | $5{\cdot}01 \pm 0{\cdot}02$ | $4{\cdot}77 \pm 0{\cdot}02$ | $0{\cdot}24 \pm 0{\cdot}04$ | $0{\cdot}21 \pm 0{\cdot}01$ | (1) |
| W | Ba | 4·54 | 2·11 | 2·43 | $2{\cdot}13 \pm 0{\cdot}05$ | (2) |

*References to Table 4*

(1) Glasoe, *Phys. Rev.* **38**, 1490 (1931).
(2) Anderson, *Phys. Rev.* **47**, 958 (1935).

We would emphasize that the Volta potential difference $\phi^{Ae} - \phi^{Be}$ is the electrostatic potential difference between two places in the vapour, and this is the only precise meaning that one can attach to the so-called contact potential difference. None of our formulae involve the electrostatic potential difference between the interiors of the two metals, a quantity which is

inaccessible to measurement. This is an instructive example of the rule that potential differences are measurable only between two points in phases of the same (or almost the same) chemical composition.*

If we ever have a sufficiently detailed knowledge of the configuration of the nuclei and electrons in the interior and surface of a metal, it may be possible to compute the electric moment per unit area at metal-metal or metal-vapour interfaces. This would give the electrostatic potential difference between the interior of the two metals. At present we are completely ignorant not only of the magnitude but even of the sign of these electric double layers.

* See Gibbs, *Collected Works* (Longmans, 1928), p. 429; Guggenheim, *J. Phys. Chem.* **33**, 842 (1929).

# CHAPTER XII

## CHEMICAL KINETICS

**§ 1200. Introduction.** The subject of chemical kinetics strictly lies outside the province of this book. Equilibrium theory alone gives no information as to how equilibrium is attained. Nevertheless, equilibrium theory can be a useful tool for dealing with this problem, if combined with certain assumptions concerning the mechanisms involved. We therefore include a survey of such use of equilibrium theory, and shall lay particular stress on the assumptions involved, as these are too frequently ignored in discussions of reaction kinetics. We shall confine ourselves almost entirely to gaseous reactions. We shall exclude from consideration photochemical reactions, that is to say, reactions whose rate depends observably on radiation. We shall also exclude heterogeneous reactions, that is to say reactions occurring primarily at a solid or liquid surface. Though such surface catalysis by the walls of the container dominates many gaseous reactions, a considerable number of homogeneous gaseous reactions are known.*

When the homogeneity of a reaction has been established, its rate is studied as a function of the temperature and the concentrations. When this rate, expressed in numbers of molecules per unit time, is compared with the number of collisions per unit time, two striking facts emerge. First the number of molecules reacting in unit time is extremely small compared with the number of collisions per unit time; the ratio is usually of the order $10^{-8}$ or less, so that at most one collision in $10^{8}$ leads to chemical reaction. We shall give a numerical example later. The other important fact is the strikingly large temperature variation of the reaction rates. Whereas the total number of collisions varies as $T^{\frac{1}{2}}$, that is hardly at all over wide ranges of temperature, the reaction rate ordinarily doubles for a rise of temperature of only 10 deg. or less. These two facts suggest at once that the effective collisions are selected not from all collisions, but only from collisions with more than a certain large minimum of distributable energy. This theory is universally accepted.

The fundamental problems of chemical kinetics reduce to the following:

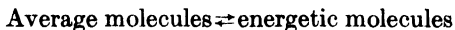
(1) What conditions, energetic or otherwise, must be satisfied by molecules so as to react?

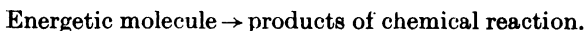
(2) How often are these conditions satisfied?

* For a general account see Hinshelwood, *The Kinetics of Chemical Change in Gaseous Systems*, Ed. 3 (Oxford, 1933); Kassel, *Kinetics of Homogeneous Gas Reactions* (Chemical Catalog Co., 1932).

The first is a problem of quantum theory, soluble in principle, but owing to its mathematical complexity insoluble in practice. At present we have to appeal to experiment for its answer. In other words, we guess the conditions necessary for reaction, try to calculate the frequency of their occurrence, and compare this with the observed rate of reaction. It is in the second problem that equilibrium theory is used to estimate the frequency of occurrence of the assumed conditions for chemical reaction. Generally speaking, these conditions include the occurrence of collisions of specified types between pairs of molecules. The procedure is to derive a formula for the number of collisions of specified type between molecules of the reacting species at complete equilibrium, and to assume that this gives an adequate approximation to the number of such collisions when the reaction is actually taking place. This approximation will be adequate provided that the reaction proceeds sufficiently slowly. The necessity for this condition was pointed out long ago by Marcelin.*

Let us examine more closely what we mean by "sufficiently slowly" for the chemical reaction not to disturb seriously the number of collisions of specified type calculated according to the equilibrium theory. All reactions of course proceed to their equilibrium point, at which all the considerations of the equilibrium theory must apply. But in chemical kinetics we are concerned with the speed of unbalanced reactions proceeding primarily in one direction, and it is these which we try to record by observation. In order to calculate such speeds from the equilibrium theory, we have to assume that certain types of collisions are effective, and that these types occur (in spite of the one-sided reaction) with a frequency corresponding to that which would be deduced from the properties of an equilibrium state. Now we shall find that the types of collisions that are of importance are those between pairs of molecules, at least one of which has considerably more energy than the average molecule. The essential condition for the usefulness of the procedure adopted is therefore that the equilibrium between those molecules of the reacting species with average energy and those with a considerable excess of energy should be effectively maintained in spite of the chemical reaction which tends to deplete the number of highly energetic molecules of the reacting species. In other words it is required that processes of the type

$$\text{Average molecules} \rightleftarrows \text{energetic molecules}$$

should be considerably faster than the process

$$\text{Energetic molecule} \rightarrow \text{products of chemical reaction.}$$

More detailed discussion of this requirement must be postponed until a later section. The experimental evidence indicates that it is usually satisfied

* Marcelin, *Ann. Physique*, 3, 164 (1915).

at least fairly well for those chemical reactions which are slow enough to be studied under normal conditions. We shall therefore provisionally assume the condition to be satisfied, and shall later try, with only limited success, to examine whether it should be so theoretically.

As a preliminary step we shall derive formulae for the number of collisions of specified types at complete equilibrium. At the ordinary low pressures used in the study of homogeneous gaseous reactions, we may apply classical statistics.

**§ 1201. Collisions classed according to translational motion.** We begin by calculating the frequency of collisions of specified type, classed entirely according to the translational motion of the molecules. At this stage we ignore the internal degrees of freedom of the molecules, and for convenience treat the molecules as rigid spheres.

Let us examine the chances of collision between two molecules having masses $m_1$, $m_2$ and diameters $D_1$, $D_2$, enclosed in a container *of unit volume.* At the instant of contact the centre of the second molecule will evidently have to lie on the surface of a sphere of radius $D_{12} = \frac{1}{2}(D_1 + D_2)$, with centre at the centre of the first molecule. We now consider especially collisions in which the relative velocity has a given magnitude $V$, and the angle between this relative velocity and the line of centres at the instant of contact lies between $\theta$ and $\theta + d\theta$. For a given relative velocity, the centre of the second molecule will then have to lie on a ring of area $2\pi D_{12}^2 \sin\theta\, d\theta$ on the surface of the sphere of radius $D_{12}$. But the component relative velocity parallel to the line of centres and hence perpendicular to the surface of this ring is $V\cos\theta$; consequently the condition for such a collision to occur within the time interval $dt$ is that the centre of the second molecule should lie within a specified volume $2\pi D_{12}^2 \sin\theta\, d\theta\,.\,V\cos\theta\, dt$. But the fraction of time that the centre of a molecule will occupy this element of volume is equal to the ratio of this volume to the whole available volume, in this case unity. Hence the chance for such collisions per unit time is $2\pi D_{12}^2 V \sin\theta \cos\theta\, d\theta$ for any pair of molecules moving with a relative velocity of given magnitude $V$. This result is independent of the direction in space of the relative velocity.

We now consider an assembly of unspecified volume containing $\nu_1$, $\nu_2$ molecules of types 1, 2 respectively per unit volume. Then the number of molecules per unit volume of type 1 with velocity components in the ranges $u, u+du$; $v, v+dv$; $w, w+dw$ is by (303, 3)

$$\nu_1\left(\frac{m_1}{2\pi kT}\right)^{\frac{3}{2}} e^{-\frac{1}{2}m_1c_1^2/kT}\, du_1\, dv_1\, dw_1, \qquad (1201, 1)$$

where $c_1$ is the magnitude of the resultant velocity of the molecule 1, so that

$$c_1^2 = u_1^2 + v_1^2 + w_1^2. \qquad (1201, 2)$$

*Similar formulae hold for the molecules of type* 2. The number of pairs of *molecules of types 1* and 2 per unit volume is $\nu_1\nu_2/\sigma_{12}$, where the symmetry number $\sigma_{12}$ is 2 if the types of the two molecules are the same and is unity otherwise. Hence, using (1) and a similar formula for the molecules of type 2, the number of pairs of molecules with velocity components in the ranges $u_1, u_1+du_1$; $v_1, v_1+dv_1$; $w_1, w_1+dw_1$ and $u_2, u_2+du_2$; $v_2, v_2+dv_2$; $w_2, w_2+dw_2$ respectively is

$$\frac{\nu_1\nu_2}{\sigma_{12}}\frac{(m_1m_2)^{\frac{3}{2}}}{(2\pi kT)^3}e^{-(\frac{1}{2}m_1c_1^2+\frac{1}{2}m_2c_2^2)/kT}du_1dv_1dw_1du_2dv_2dw_2. \quad (1201, 3)$$

Each such pair has a relative velocity $V$ given by

$$V^2 = (u_1-u_2)^2+(v_1-v_2)^2+(w_1-w_2)^2, \quad (1201, 4)$$

and makes a number of collisions per unit time equal to $2\pi D_{12}^2V\sin\theta\cos\theta d\theta$. The total number of collisions per unit volume and per unit time with velocity components in the specified ranges, and the angle between $V$ and the line of centres at impact lying in the range $\theta, \theta+d\theta$, is therefore

$$\frac{\nu_1\nu_2}{\sigma_{12}}\frac{(m_1m_2)^{\frac{3}{2}}}{(2\pi kT)^3}e^{-(\frac{1}{2}m_1c_1^2+\frac{1}{2}m_2c_2^2)/kT}2\pi D_{12}^2V\sin\theta\cos\theta du_1dv_1dw_1du_2dv_2dw_2d\theta. \quad (1201.5)$$

We now introduce new variables $u$, $v$, $w$, $\alpha$, $\beta$, $\gamma$ defined by

$$u = \frac{m_1u_1+m_2u_2}{m_1+m_2}, \quad v = \frac{m_1v_1+m_2v_2}{m_1+m_2}, \quad w = \frac{m_1w_1+m_2w_2}{m_1+m_2}; \quad (1201, 6)$$

$$\alpha = u_2-u_1, \quad \beta = v_2-v_1, \quad \gamma = w_2-w_1, \quad (1201, 7)$$

so that $u$, $v$, $w$ are the velocity components of the centre of mass of the two molecules, and $\alpha$, $\beta$, $\gamma$ are the components of their relative velocity. If we denote by $c$ the magnitude of the resultant velocity of the centre of mass and by $V$ the magnitude of the resultant relative velocity, we have

$$c^2 = u^2+v^2+w^2, \quad (1201, 8)$$

$$V^2 = \alpha^2+\beta^2+\gamma^2. \quad (1201, 9)$$

It may then be verified that

$$m_1c_1^2+m_2c_2^2 = (m_1+m_2)c^2+\mu V^2, \quad (1201, 10)$$

where $\mu$, called the reduced mass of the pair, is given by

$$\mu = \frac{m_1m_2}{m_1+m_2}. \quad (1201, 11)$$

It can also be shown that

$$du_1du_2 = dud\alpha, \quad dv_1dv_2 = dvd\beta, \quad dw_1dw_2 = dwd\gamma. \quad (1201, 12)$$

Using (8)–(12) we can transform (3) to

$$\frac{\nu_1 \nu_2}{\sigma_{12}} \frac{(m_1 m_2)^{\frac{3}{2}}}{(2\pi kT)^3} e^{-\{\frac{1}{2}(m_1+m_2)c^2+\frac{1}{2}\mu V^2\}/kT}\, 2\pi D_{12}^2 V \sin\theta \cos\theta\, du\, dv\, dw\, d\alpha\, d\beta\, d\gamma\, d\theta. \tag{1201, 13}$$

We now wish to integrate $du\,dv\,dw$ over all possible directions for the velocity $c$ of the centre of mass, and to integrate $d\alpha\,d\beta\,d\gamma$ over all possible directions for the relative velocity $V$. To do so we first transform to spherical polar coordinates so that $du\,dv\,dw$ becomes $c^2 dc\,d\Omega$ and $d\alpha\,d\beta\,d\gamma$ becomes $V^2 dV\,d\omega$, where $\Omega$ and $\omega$ denote solid angles. The angle $\theta$ between $V$ and the line of centres at impact is variable independently of the directions of both $c$ and $V$. We can therefore immediately integrate over all directions of $c$ and of $V$. Integrations with respect to $d\Omega$ and $d\omega$ over all directions independently each give a factor $4\pi$. We find therefore that the number of collisions per unit volume and per unit time, such that the velocity of the centre of mass lies in the range $c, c+dc$, the relative velocity lies in the range $V, V+dV$, while the angle between the relative velocity and the line of centres lies in the range $\theta, \theta+d\theta$, is

$$\frac{\nu_1 \nu_2}{\sigma_{12}} \frac{(m_1 m_2)^{\frac{3}{2}}}{(2\pi kT)^3} e^{-\{\frac{1}{2}(m_1+m_2)c^2+\frac{1}{2}\mu V^2\}/kT}\, 32\pi^3 D_{12}^2 c^2 V^3 \sin\theta \cos\theta\, dc\, dV\, d\theta. \tag{1201, 14}$$

Integrating over all values of $c$ from zero to infinity, we obtain for the number of collisions per unit volume and per unit time, in which the relative velocity lies in the range $V, V+dV$, and the angle between the relative velocity and the line of centres at the instant of contact lies in the range $\theta, \theta+d\theta$, the expression

$$\frac{\nu_1 \nu_2}{\sigma_{12}} \left(\frac{\mu}{2\pi kT}\right)^{\frac{3}{2}} e^{-\frac{1}{2}\mu V^2/kT}\, 8\pi^2 D_{12}^2 V^3 \sin\theta \cos\theta\, dV\, d\theta. \tag{1201, 15}$$

For the molecules to be approaching $\theta$ must lie between 0 and $\frac{1}{2}\pi$. If then we integrate (15) over $\theta$ from 0 to $\frac{1}{2}\pi$, we obtain for the number of collisions per unit volume and per unit time, in which the magnitude of the relative velocity lies in the range $V, V+dV$,

$$\frac{\nu_1 \nu_2}{\sigma_{12}} \left(\frac{\mu}{2\pi kT}\right)^{\frac{3}{2}} e^{-\frac{1}{2}\mu V^2/kT}\, 4\pi^2 D_{12}^2 V^3 dV. \tag{1201, 16}$$

Alternatively the number of collisions per unit volume and per unit time, with relative translational energy $\epsilon = \frac{1}{2}\mu V^2$ in the range $\epsilon, \epsilon+d\epsilon$, is given by

$$\frac{\nu_1 \nu_2}{\sigma_{12}} \left(\frac{2\pi kT}{\mu}\right)^{\frac{1}{2}} e^{-\epsilon/kT}\, 2D_{12}^2 \frac{\epsilon}{kT} \frac{d\epsilon}{kT}. \tag{1201, 17}$$

The total number $Z$ of collisions per unit volume and per unit time is obtained by integration of (17) from 0 to $\infty$. We find

$$Z = 2\frac{\nu_1\nu_2}{\sigma_{12}}D_{12}^2\left(\frac{2\pi kT}{\mu}\right)^{\frac{1}{2}}. \qquad (1201, 18)$$

Similarly for the number of collisions per unit volume and per unit time, in which the energy of relative motion exceeds a specified value $\epsilon^*$, we obtain by integration of (17) from $\epsilon^*$ to $\infty$

$$\frac{\nu_1\nu_2}{\sigma_{12}}\left(\frac{2\pi kT}{\mu}\right)^{\frac{1}{2}} 2D_{12}^2 e^{-\epsilon^*/kT}\left(\frac{\epsilon^*}{kT}+1\right) = Ze^{-\epsilon^*/kT}\left(\frac{\epsilon^*}{kT}+1\right). \qquad (1201, 19)$$

For applications to reaction rates we shall require also the number of collisions in which the translational energy in the direction of the line of centres at the moment of impact exceeds a specified value. Let us denote by $R$ the component $V\cos\theta$ of $V$ along the line of centres. Then for $R$ to exceed a specified value $R^*$ we must have for all values of $V$ and $\theta$

$$1 \geqslant \cos\theta \geqslant R^*/V, \quad V \geqslant R^*. \qquad (1201, 20)$$

To obtain the number of collisions per unit volume and per unit time for which $R$ exceeds $R^*$, we therefore integrate (15) over values of $\cos\theta$ from 1 to $R^*/V$ and then over $V$ from $R^*$ to $\infty$. The first integration affects only the factor $\cos\theta\sin\theta d\theta$ and gives

$$-\int_1^{R^*/V}\cos\theta\, d\cos\theta = \frac{1}{2}\left(1-\frac{R^{*2}}{V^2}\right).$$

The remaining integration is then

$$\int_{R^*}^{\infty}\frac{\nu_1\nu_2}{\sigma_{12}}\left(\frac{\mu}{2\pi kT}\right)^{\frac{3}{2}} e^{-\frac{1}{2}\mu V^2/kT}\, 4\pi^2 D_{12}^2 V^3\left(1-\frac{R^{*2}}{V^2}\right)dV$$

$$= \frac{\nu_1\nu_2}{\sigma_{12}}\left(\frac{2\pi kT}{\mu}\right)^{\frac{1}{2}} e^{-\frac{1}{2}\mu R^{*2}/kT}\, 2D_{12}^2$$

$$= Ze^{-\frac{1}{2}\mu R^{*2}/kT} \qquad (1201, 21)$$

Alternatively the number of collisions per unit volume and per unit time, in which the relative translational energy along the line of centres at the instant of contact exceeds a specified value $\epsilon^*$, is given by

$$Ze^{-\epsilon^*/kT}, \qquad (1201, 22)$$

and by differentiation we find that the number in the energy range $\epsilon, \epsilon+d\epsilon$ is

$$Ze^{-\epsilon/kT}\frac{d\epsilon}{kT}. \qquad (1201, 23)$$

**§ 1202. Energy of internal vibrations.** We shall now give an elementary discussion of the distribution of energy in the internal vibrations of molecules and shall derive approximate formulae. We assume that each internal vibration behaves as a linear harmonic oscillator with a characteristic frequency $\nu$. Then the fraction of time that a given oscillator has an energy $nh\nu$ relative to the energy of the lowest state is

$$e^{-nh\nu/kT}(1-e^{-h\nu/kT}). \tag{1202, 1}$$

Let us first consider oscillators for which $h\nu \gg kT$. These will be completely unexcited in the sense of § 306. We may ignore the existence of the excited vibrational states, and consequently the problem of distribution of vibrational energy does not arise.

We consider next oscillators for which $h\nu \ll kT$. In the terminology of § 306 these are classical, and (1) reduces with sufficient accuracy to

$$\frac{h\nu}{kT}e^{-nh\nu/kT}. \tag{1202, 2}$$

Alternatively we may say that the fraction of time such an oscillator has energy, relative to the normal state, in the range $nh\nu$ to $(n+dn)h\nu$ is

$$\frac{h\nu}{kT}e^{-nh\nu/kT}\,dn, \tag{1202, 3}$$

or in the energy range $\epsilon, \epsilon+d\epsilon$

$$e^{-\epsilon/kT}\frac{d\epsilon}{kT}. \tag{1202, 4}$$

There will be a third class of oscillator for which $h\nu/kT$ is comparable with unity. Simplified formulae cannot be derived for such oscillators. We must therefore as a crude approximation treat such an oscillator as belonging to the first class if $h\nu > kT$, and to the second if $h\nu < kT$. We thus treat a polyatomic molecule as having a definite number of classical vibrational modes, and a definite number of unexcited vibrational modes, their sum being equal to three times the number of atoms in the molecule less six (five for a linear molecule). As long as there are not too many frequencies comparable with $kT/h$, such an approximate treatment can be useful.

The most important quantity to be calculated is the fraction of time during which $s$ specified classical oscillators have between them an energy exceeding a given value $\epsilon^*$. By combined application of formulae such as (4) to each of the $s$ oscillators we obtain for the fraction of time during which their combined energy lies between $\epsilon$ and $\epsilon+d\epsilon$

$$(kT)^{-s}\underset{\epsilon\leqslant\epsilon_1+\epsilon_2+\dots+\epsilon_s\leqslant\epsilon+d\epsilon}{\int\dots\int} e^{-(\epsilon_1+\epsilon_2+\dots+\epsilon_s)/kT}\,d\epsilon_1\,d\epsilon_2\dots d\epsilon_s, \tag{1202, 5}$$

the integral being $(s-1)$ times multiple. Since a further integration of $d\epsilon$ from 0 to $\infty$ must give unity, we may replace (5) by

$$\frac{\underset{\epsilon<\epsilon_1+\epsilon_2+\ldots+\epsilon_s\leqslant\epsilon+d\epsilon}{\underset{(s-1)}{\int\ldots\int}} e^{-(\epsilon_1+\epsilon_2+\ldots+\epsilon_s)/kT}\,d\epsilon_1\,d\epsilon_2\ldots d\epsilon_s}{\underset{(s)}{\int\ldots\int} e^{-(\epsilon_1+\epsilon_2+\ldots+\epsilon_s)/kT}\,d\epsilon_1\,d\epsilon_2\ldots d\epsilon_s}, \tag{1202, 6}$$

the integral in the numerator being $(s-1)$ times multiple, that in the denominator $s$ times multiple. To calculate (6) we make the substitutions

$$\epsilon_1 = l_1^2\epsilon,\ \epsilon_2 = l_2^2\epsilon,\ \ldots,\ \epsilon_s = l_s^2\epsilon, \tag{1202, 7}$$

subject to

$$l_1^2+l_2^2+\ldots+l_s^2 = 1. \tag{1202, 8}$$

We may therefore regard $l_1, l_2, \ldots, l_s$ as direction cosines in an $s$-dimensional space. The integral in the numerator of (6) then extends over an $(s-1)$-dimensional hyperspherical shell of radius $\epsilon^{\frac{1}{2}}$ and thickness $d(\epsilon^{\frac{1}{2}})$, while the integral in the denominator extends over the whole $s$-dimensional space. When we transform $d\epsilon_1 d\epsilon_2\ldots d\epsilon_s$ we obtain a product containing $\epsilon^{s-1}d\epsilon$ as one factor, the other factor depending only on the $l$'s and $dl$'s. We need not write down this factor, because it will be the same in the denominator and the numerator, and when we integrate over all directions the resultant quantities will be the same in the denominator and the numerator and so may be cancelled. We need therefore retain in (6) only the factors dependent on $\epsilon$ and independent of the $l$'s. We thus obtain

$$\frac{e^{-\epsilon/kT}\,\epsilon^{s-1}\,d\epsilon}{\int_0^\infty e^{-\epsilon/kT}\,\epsilon^{s-1}\,d\epsilon} = \frac{1}{(s-1)!}\left(\frac{\epsilon}{kT}\right)^{s-1} e^{-\epsilon/kT}\,\frac{d\epsilon}{kT}. \tag{1202, 9}$$

The fraction of time during which the energy of the $s$ oscillators exceeds a specified value $\epsilon^*$ is therefore

$$\int_{\epsilon^*}^{\infty}\frac{1}{(s-1)!}\left(\frac{\epsilon}{kT}\right)^{s-1} e^{-\epsilon/kT}\,\frac{d\epsilon}{kT}. \tag{1202, 10}$$

We can evaluate (10) by successive integration by parts and obtain

$$e^{-\epsilon^*/kT}\sum_{r=0}^{s-1}\frac{1}{r!}\left(\frac{\epsilon^*}{kT}\right)^r. \tag{1202, 11}$$

We note that in (11) the ratio of any term to the previous term is $\epsilon^*/rkT$. Consequently provided $\epsilon^*\gg skT$ we may reject all terms of (11) except the last and obtain the approximation

$$\frac{1}{(s-1)!}\left(\frac{\epsilon^*}{kT}\right)^{s-1} e^{-\epsilon^*/kT} \qquad (\epsilon^*\gg skT). \tag{1202, 12}$$

The condition for this approximation is sometimes given as $\epsilon^* \gg kT$. In applications $s$ may be 10 or more, and the approximation would then be bad if $\epsilon^* \simeq 10kT$. It is therefore safer to write the condition as $\epsilon^* \gg s\,kT$.

**§ 1203. Collisions involving internal energy.** We can now combine the results of the two previous sections to classify collisions according to the internal vibrational energies as well as the translational energies of the molecules involved. Let us first derive the number of collisions classified according to the sum of the relative kinetic energy *along the line of centres* at the instant of contact and the energy of $s$ specified internal vibrations. By combining (1201, 22) and (1202, 9) we find for the number of collisions per unit volume and per unit time, in which the relative kinetic energy along the line of centres lies in the range $\epsilon_1, \epsilon_1 + d\epsilon_1$, while the energy in $s$ specified vibrations belonging to one or both of the molecules lies in the range $\epsilon_2, \epsilon_2 + d\epsilon_2$,

$$Ze^{-\epsilon_1/kT}\frac{d\epsilon_1}{kT}\frac{1}{(s-1)!}\left(\frac{\epsilon_2}{kT}\right)^{s-1}e^{-\epsilon_2/kT}\frac{d\epsilon_2}{kT}, \tag{1203, 1}$$

where $Z$ is given by (1201, 18) and is consequently independent of $\epsilon_1, \epsilon_2$. We now make the substitutions

$$\epsilon_1 + \epsilon_2 = \epsilon, \quad \epsilon_2 = \eta, \tag{1203, 2}$$

and obtain

$$Ze^{-\epsilon/kT}\frac{1}{(s-1)!}\left(\frac{\eta}{kT}\right)^{s-1}\frac{d\epsilon}{kT}\frac{d\eta}{kT}. \tag{1203, 3}$$

If we integrate (3) with respect to $\eta$ from 0 to $\epsilon$, we obtain for the number of collisions per unit volume and per unit time, in which the sum of the relative kinetic energy along the line of centres and the energy in $s$ specified internal vibrations lies in the range $\epsilon, \epsilon + d\epsilon$, the expression

$$Ze^{-\epsilon/kT}\frac{1}{s!}\left(\frac{\epsilon}{kT}\right)^{s}\frac{d\epsilon}{kT}. \tag{1203, 4}$$

Hence the number of collisions per unit volume and per unit time, in which the sum of the relative kinetic energy along the line of centres and the energy in $s$ specified internal vibrations exceeds a given value $\epsilon^*$, is given by

$$\int_{\epsilon^*}^{\infty} Ze^{-\epsilon/kT}\frac{1}{s!}\left(\frac{\epsilon}{kT}\right)^{s}\frac{d\epsilon}{kT} = Ze^{-\epsilon^*/kT}\sum_{r=0}^{s}\frac{1}{r!}\left(\frac{\epsilon^*}{kT}\right)^{r} \tag{1203, 5}$$

by repeated integration by parts. Provided $\epsilon^* \gg s\,kT$ (the condition $\epsilon^* \gg kT$ is insufficient), we may replace (5) by its last term

$$Ze^{-\epsilon^*/kT}\frac{1}{s!}\left(\frac{\epsilon^*}{kT}\right)^{s}. \tag{1203, 6}$$

We can similarly obtain formulae for the number of collisions classified according to the sum of the *total* relative kinetic energy and the energy of $s$ specified internal vibrations. For the number of collisions per unit volume and per unit time in which the total relative kinetic energy lies in the range $\epsilon_1, \epsilon_1 + d\epsilon$, while the energy in $s$ specified internal vibrations lies in the range $\epsilon_2, \epsilon_2 + d\epsilon_2$, we obtain, by combining (1201, 17), (1201, 18) and (1202, 9), the expression

$$Ze^{-\epsilon_1/kT}\frac{\epsilon_1}{kT}\frac{d\epsilon_1}{kT}\frac{1}{(s-1)!}\left(\frac{\epsilon_2}{kT}\right)^{s-1}e^{-\epsilon_2/kT}\frac{d\epsilon_2}{kT}. \qquad (1203, 7)$$

By using the substitutions (2) and integrating with respect to $\eta$, from 0 to $\epsilon$, we obtain for the number of collisions per unit volume and per unit time, in which the sum of the total relative translational energy and the energy of $s$ specified internal vibrations lies in the range $\epsilon, \epsilon + d\epsilon$,

$$Ze^{-\epsilon/kT}\frac{d\epsilon}{kT}\int_0^\epsilon \frac{1}{(s-1)!}\left(\frac{\epsilon-\eta}{kT}\right)\left(\frac{\eta}{kT}\right)^{s-1}\frac{d\eta}{kT}$$

$$= Ze^{-\epsilon/kT}\frac{1}{(s+1)!}\left(\frac{\epsilon}{kT}\right)^{s+1}\frac{d\epsilon}{kT}. \qquad (1203, 8)$$

For the number of collisions per unit volume and per unit time, in which the sum of the total relative translational energy and the energy in $s$ specified internal vibrations exceeds a given value $\epsilon^*$, we have

$$\int_{\epsilon^*}^{\infty} Ze^{-\epsilon/kT}\frac{1}{(s+1)!}\left(\frac{\epsilon}{kT}\right)^{s+1}\frac{d\epsilon}{kT} = Ze^{-\epsilon^*/kT}\sum_{r=0}^{s+1}\frac{1}{r!}\left(\frac{\epsilon^*}{kT}\right)^r, \qquad (1203, 9)$$

by repeated integration by parts. Provided $\epsilon^* \gg s\,kT$ (the condition $\epsilon^* \gg kT$ is insufficient), we may replace (9) by its last term, and obtain the approximation

$$Ze^{-\epsilon^*/kT}\frac{1}{(s+1)!}\left(\frac{\epsilon^*}{kT}\right)^{s+1}. \qquad (1203, 10)$$

A comparison of (8), (9) with (4), (5) respectively shows that we have the same distribution laws for either the sum of the relative translational energy *along the line of centres* and $s$ vibrations or for the sum of the *total* relative translational energy and $(s-1)$ vibrations. The reason for this is that, as the vibrational degrees of freedom are effectively classical, each contributes two square terms to the energy, while each of the two transverse relative translations, having only kinetic energy associated with it, contributes one square term to the energy. Thus as regards partition of energy the two transverse translational degrees of freedom together make the same contribution as a single classical internal vibration.

We can, if we wish, extend our formulae to include classical rotational degrees of freedom. Each pair of rotational degrees of freedom will contribute two square terms to the energy and is in this respect analogous to one classical vibrational degree of freedom. If we denote by $t$ the total number of square terms contributing to the energy $\epsilon^*$, then, if $t$ is even, the number of collisions per unit volume and per unit time, in which the sum of the translational energy along the line of centres and the energy in $t$ specified square terms exceeds a given value $\epsilon^*$, is

$$Z\epsilon^{-\epsilon^*/kT}\sum_{r=0}^{\frac{1}{2}t}\frac{1}{\Gamma(r+1)}\left(\frac{\epsilon^*}{kT}\right)^r. \qquad (1203, 11)$$

Formula (11) is a mere transcription of (5). When $t$ is odd, one obtains instead of (5)

$$Ze^{-\epsilon^*/kT}\left\{\sum_{r=\frac{1}{2}}^{\frac{1}{2}t}\frac{1}{\Gamma(r+1)}\left(\frac{\epsilon^*}{kT}\right)^r + O\left(\frac{\epsilon^*}{kT}\right)^{-\frac{1}{2}}\right\}, \qquad (1203, 12)$$

and the terms of order $(\epsilon^*/kT)^{-\frac{1}{2}}$ are usually negligible in applications.

**§ 1204. Classification of reactions.** Chemical reactions which proceed sufficiently slowly for their rates to be measured can be classed in three distinct ways which must not be confused.

(*a*) According to the number of reactant molecules in the stoichiometric formula describing the reaction.

(*b*) According to the number of concentrations of gaseous components, to the product of which the rate is proportional.

(*c*) According to the number of molecules taking part in each elementary mechanism leading to chemical change.

The first classification is useful in discussing the equilibrium between balanced reactions, but has in general no simple or obvious connection with the rate of either reaction.

By the second classification we define a reaction as being of the $n$th order if its rate is directly proportional to the product of $n$ concentrations. Thus suppose the rate of decomposition of molecules $A$ is given by

$$\frac{\partial \nu_A}{\partial t} = -k_n(\nu_A)^{n_A}(\nu_B)^{n_B}\ldots, \qquad (1204, 1)$$

where

$$n_A + n_B + \ldots = n, \qquad (1204, 2)$$

and $k_n$ depends on the temperature but is independent of the concentrations, then the reaction is said to be of $n$th order ($n_A$th order with respect to $A$, $n_B$th order with respect to $B$ and so on), and $k_n$ is called the $n$th order rate constant. It is often found that $n$ is a small integer, but sometimes $n$ is

fractional, and sometimes the rate cannot be expressed in the form (1) at all. For a first order reaction

$$\frac{\partial \nu_A}{\partial t} = -k_1 \nu_A \tag{1204, 3}$$

the rate constant $k_1$ is a frequency. For a second order reaction

$$\frac{\partial \nu_A}{\partial t} = -k_2 \nu_A \nu_B \quad \text{or} \quad \frac{\partial \nu_A}{\partial t} = -k_2 \nu_A^2 \tag{1204, 4}$$

the rate constant $k_2$ has the dimensions frequency/concentration.

In respect of the third classification we can define the two following important types of mechanism of chemical processes:

*Bimolecular mechanism.* A normal molecule $A$, by collision or otherwise, acquires a considerable excess of energy. We shall denote such a molecule by $A'$ and refer to it as an energetic molecule. The energetic molecule $A'$ collides with an average molecule $B$ or an energetic molecule $B'$ (of the same or of a different chemical nature). If the collision is favourable with respect to the energies and relative configurations of the two molecules, the molecule $A'$ on collision with $B$ or $B'$ decomposes. The other molecule $B$ or $B'$ may or may not also decompose. The combined pair of molecules $A'$ and $B$ or $A'$ and $B'$, at the instant that $A'$ is on the point of decomposing, we call the reacting complex, and we denote it by $AB^*$.

*Unimolecular mechanism.* A normal molecule $A$, by collision or otherwise, is converted to an energetic molecule $A'$. The energetic molecule $A'$, provided it is left long enough undisturbed by collision or other external influence, spontaneously decomposes. The molecule at the instant it is on the point of decomposing we call the reacting molecule, and we denote it by $A^*$.

In general there is no simple connection between the *molecularity* of the mechanism (unimolecular or bimolecular) and the *order* of the reaction (first, second, etc.). This can be illustrated by three familiar examples:

(1) The reaction $2NO + O_2 \rightarrow 2NO_2$ is of the third order (second order in NO and first order in $O_2$), but the mechanism is probably bimolecular between $N_2O_2$ and $O_2$.

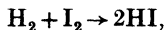
(2) The balanced reactions $H_2 + D_2 \rightleftarrows 2HD$ are each of the order $\frac{3}{2}$, but the mechanism is bimolecular between one of the molecules $H_2$, $D_2$, HD and one of the atoms H, D.

(3) The decomposition of several ethers is first order at ordinary pressures but becomes second order at very low pressures, while the mechanism is believed to be unimolecular.

It is generally, if not universally, agreed that all those gaseous reactions whose rate has been measured can be accounted for by bimolecular and

unimolecular mechanisms. Many reactions are complicated, taking place in several steps, but each step either is a rapidly attained equilibrium or, if slow, is itself a bimolecular or a unimolecular mechanism. Often one particular step is much slower than all the others and in this case the rate of the reaction is determined by the rate of this step, all the remaining steps being treated as equilibria. In this case the reaction will be of a simple, but not necessarily integral, order. If on the other hand there is no single step so much slower than all the others as to be the only rate determining step, it will usually not be possible to describe the rate by a formula of the type (1). It would take us too far to discuss how the resultant rate of such a complicated reaction depends on the rates of the component steps. Our primary interest is in the rate of the component slow processes and we may therefore for the present suppose that the reaction is simple and that only one such slow mechanism is involved. We shall now proceed to discuss separately bimolecular and unimolecular mechanisms.

**§ 1205. Bimolecular reactions of second order.** For the sake of simplicity we shall consider a reaction involving only one step, this being a bimolecular mechanism. The best studied examples are

$$H_2 + I_2 \rightarrow 2HI,$$

and the converse reaction

$$2HI \rightarrow H_2 + I_2.$$

At the present stage we assume that the collisions which lead to reaction do not appreciably diminish the number of energetic molecules which are required to form a reacting complex. This assumption will be discussed in § 1211. Subject to this assumption the rate is obtained by calculating the number of collisions of each type according to the equilibrium formulae, multiplying by a probability factor for reaction, and integrating over all types of collision. We shall first write down the most general formulae without specifying the value of the probability factor for each type of collision, and shall then derive more specialized formulae depending on the values assigned to these probability factors. In doing this it is more convenient to start with a more general formulation than we used in § 1202.

It is physically obvious that the probability for reaction of two molecules on colliding is determined by the energy of their relative translational motion and their internal (including rotational) energies, whereas the translational energy of their centre of mass is irrelevant. Now the number of collisions per unit volume and per unit time, in which the relative velocity lies in the range $V, V+dV$, and the angle between the relative velocities

and the line of centres at the instant of contact lies in the range $\theta, \theta+d\theta$, is given by formula (1201, 15), which can be written in the alternative form

$$\frac{\nu_1\nu_2}{\sigma_{12}}\left(\frac{2\pi kT}{\mu}\right)^{\frac{1}{2}} 4D_{12}^2 \sin\theta \cos\theta\, d\theta\, e^{-\epsilon_{12}/kT}\frac{\epsilon_{12}}{kT}\frac{d\epsilon_{12}}{kT}, \qquad (1205, 1)$$

where

$$\epsilon_{12} = \tfrac{1}{2}\mu V^2 \qquad (1205, 2)$$

is the relative translational kinetic energy of the two molecules. The number of these collisions in which the molecule 1 is in its $q$th internal state of energy $\eta_q$, and the molecule 2 in its $r$th internal state of energy $\zeta_r$ (degenerate states being counted multiply), is therefore

$$\frac{\nu_1\nu_2}{\sigma_{12}}\left(\frac{2\pi kT}{\mu}\right)^{\frac{1}{2}} 4D_{12}^2 \sin\theta \cos\theta\, d\theta\, e^{-\epsilon_{12}/kT}\frac{\epsilon_{12}}{kT}\frac{d\epsilon_{12}}{kT}\frac{e^{-\eta_q/kT}}{\sum_q e^{-\eta_q/kT}}\frac{e^{-\zeta_r/kT}}{\sum_r e^{-\zeta_r/kT}}. \qquad (1205, 3)$$

If $\kappa$ denotes the probability that a collision of this type results in chemical reaction, $\kappa$ being a function of $\epsilon_{12}$ (or $V$), $\theta$ and the internal states of both molecules, the number of collisions per unit volume and per unit time resulting in reaction is obtained by multiplying (3) by $\kappa$ and integrating over all types of collisions; we obtain

$$\frac{\dfrac{\nu_1\nu_2}{\sigma_{12}}\left(\dfrac{2\pi kT}{\mu}\right)^{\frac{1}{2}}\dfrac{4D_{12}^2}{(kT)^2}\displaystyle\int d\theta\int \epsilon_{12}\,d\epsilon_{12}\sum_q\sum_r \kappa \sin\theta\cos\theta\, e^{-(\epsilon_{12}+\eta_q+\zeta_r)/kT}}{\sum_q e^{-\eta_q/kT}\sum_r e^{-\zeta_r/kT}}. \qquad (1205, 4)$$

Since the number of reactive collisions per unit volume and per unit time is proportional to $\nu_1\nu_2$, the reaction is of the second order and the second order rate constant $k_2$ is given by

$$k_2 = \frac{\left(\dfrac{2\pi kT}{\mu}\right)^{\frac{1}{2}}\dfrac{4D_{12}^2}{(kT)^2}\displaystyle\int d\theta\int \epsilon_{12}\,d\epsilon_{12}\sum_q\sum_r \kappa \sin\theta\cos\theta\, e^{-(\epsilon_{12}+\eta_q+\zeta_r)/kT}}{\sum_q e^{-\eta_q/kT}\sum_r e^{-\zeta_r/kT}}. \qquad (1205, 5)$$

In omitting the symmetry number we have assumed either that the two colliding molecules are of different chemical species or, if they are of the same chemical species, that both react. In the exceptional case that they are of the same chemical species but only one of them decomposes (autocatalysis), there will be an extra factor $\frac{1}{2}$.

Formula (5) is of general validity, but does not predict anything definite as long as the form of $\kappa$ is left unspecified. We can, however, derive from (5) an interesting relation for the temperature dependence of the rate constant

$k_2$. If we take logarithms and differentiate with respect to $T$, we obtain

$$kT^2 \frac{\partial \log k_2}{\partial T} = \frac{\int d\theta \int \epsilon_{12} d\epsilon_{12} \Sigma_q \Sigma_r (\epsilon_{12} + \eta_q + \zeta_r) \kappa \sin\theta \cos\theta \, e^{-(\epsilon_{12}+\eta_q+\zeta_r)/kT}}{\int d\theta \int \epsilon_{12} d\epsilon_{12} \Sigma_q \Sigma_r \kappa \sin\theta \cos\theta \, e^{-(\epsilon_{12}+\eta_q+\zeta_r)/kT}} - \left\{ \tfrac{3}{2}kT + \frac{\Sigma_q \eta_q e^{-\eta_q/kT}}{\Sigma_q e^{-\eta_q/kT}} + \frac{\Sigma_r \zeta_r e^{-\zeta_r/kT}}{\Sigma_r e^{-\zeta_r/kT}} \right\}. \quad (1205, 6)$$

Now the first term on the right of (6) is the average for all reacting complexes of the sum of the relative translational energy and the two internal energies; if we add another $\frac{3}{2}kT$, it becomes the average for all reacting complexes of the total energy, translational and internal. If we add similarly $\frac{3}{2}kT$ to the first term inside the brackets, we obtain $3kT$ which is the average of the sum of the kinetic energies of any pair of molecules. The second and third terms inside the brackets are the average values of the internal energies for all molecules of each type. We can therefore express (6) in the form

$$kT^2 \frac{\partial \log k_2}{\partial T} = \text{(average total energy of reacting complexes)} - \text{(average total energy for all pairs of molecules, one of type 1 and the other of type 2)}. \quad (1205, 7)$$

This striking result is due to Tolman,* who, however, gave it in a different but equivalent form

$$kT^2 \frac{\partial \log k_2}{\partial T} - \tfrac{1}{2}kT = \text{(average total energy of reacting complexes)} - \text{(average total energy for all pairs of colliding molecules)}. \quad (1205, 8)$$

To establish the equivalence of (7) and (8) it is sufficient to show that the average total translational energy per pair of colliding molecules exceeds twice the average kinetic energy per molecule by $\frac{1}{2}kT$. This requires us to show that the average relative translational energy per pair of colliding molecules is $2kT$. The reason for this excess is, of course, that fast molecules collide more often than slow ones. Now the number of collisions with relative translational energy in the range $\epsilon, \epsilon + d\epsilon$ is according to (1201, 17) proportional to $e^{-\epsilon/kT} \epsilon d\epsilon$, and consequently the average value for the relative translational energy of colliding molecules is

$$\frac{\int_0^\infty e^{-\epsilon/kT} \epsilon^2 d\epsilon}{\int_0^\infty e^{-\epsilon/kT} \epsilon d\epsilon} = 2kT. \quad (1205, 9)$$

This establishes the equivalence of (7) and (8).

* Tolman, *J. Am. Chem. Soc.* **42**, 2506 (1920).

The term "activation energy" (or "heat of activation") for bimolecular processes is used sometimes to denote each side of equation (7), and at others to denote each side of equation (8). As long as there is no agreement as to its meaning, it is best to avoid using the term for bimolecular processes.

If it is assumed empirically that each side of equation (7) is independent of temperature, we can integrate (7) and obtain

$$k_2 = Pe^{-Q/kT} \qquad (P, Q \text{ independent of } T), \qquad (1205, 10)$$

where either side of equation (7) is equal to $Q$. This is the semi-empirical equation of Arrhenius. All experimental data on gaseous bimolecular reactions can be fitted by a formula of this type by assigning suitable values to the constants $P$, $Q$. Owing, however, to the shortness of the temperature range over which any one reaction can be conveniently studied, the data can be fitted equally well by a formula of the form

$$k_2 = PT^r e^{-Q/kT} \qquad (P, r, Q \text{ independent of } T), \qquad (1205, 11)$$

with an arbitrary small positive or negative value assigned to $r$. In particular they can be fitted by the equation

$$k_2 = PT^{\frac{1}{2}} e^{-Q/kT} \qquad (P, Q \text{ independent of } T), \qquad (1205, 12)$$

which is obtained by integration of (8), assuming empirically that each side of (8) is independent of the temperature and equal to $Q$.

There is no *a priori* reason for assuming either that the two sides of (7) are independent of temperature or that the two sides of (8) are independent of temperature, and consequently neither formula (10) nor formula (12) is *a priori* more fundamental than the more general formula (11). Actually we can derive theoretically various formulae approximating to the form (11) with various values of $r$ by making various assumptions concerning the number of degrees of freedom contributing to the excess energy required for reaction to take place.

Let us first arbitrarily make the assumption concerning $\kappa$, the probability for reaction occurring in (5), that $\kappa$ has a constant value $\alpha$ when the sum of the *total* relative translational energy and the internal energy in $s$ specified vibrational modes of one or both molecules exceeds a specified value $\epsilon^*$ and is otherwise zero; this implies, of course, that $\kappa$ is independent of $\theta$. This assumption enables us to perform the integrations in (5). We need not go through the details, as we have already derived formula (1203, 9) for the number of collisions per unit volume and per unit time in which the sum of the total relative translational energy and the energy in $s$ specified internal vibrations exceeds a given value $\epsilon^*$. Hence by com-

parison of (1201, 18) and (1203, 9) we find that our assumption leads to a second order rate constant $k_2$ given by

$$k_2 = 2\alpha D^2\left(\frac{2\pi kT}{\mu}\right)^{\frac{1}{2}} e^{-\epsilon^*/kT} \sum_{r=0}^{s+1} \frac{1}{r!}\left(\frac{\epsilon^*}{kT}\right)^r, \qquad (1205, 13)$$

where we now write $D$ instead of $D_{12}$ for the mean collision diameter. Provided $\epsilon^* \gg skT$ (the condition $\epsilon^* \gg kT$ is insufficient) we may replace (13) by the approximation

$$k_2 \simeq 2\alpha D^2\left(\frac{2\pi kT}{\mu}\right)^{\frac{1}{2}} \frac{1}{(s+1)!}\left(\frac{\epsilon^*}{kT}\right)^{s+1} e^{-\epsilon^*/kT}, \qquad (1205, 14)$$

which is of the form (11) with $Q = \epsilon^*$ and $r = -(s+\frac{1}{2})$.

If we now make the alternative assumption concerning $\kappa$, the probability for reaction, that $\kappa$ has a constant value $\alpha$ provided the sum of the translational kinetic energy *in the direction of the line of centres* and the internal energy in $s$ specified vibrational modes of one or both molecules exceeds a specified value $\epsilon^*$, we obtain a slightly different result. We have now to use formula (1203, 5) instead of (1203, 9) and we obtain

$$k_2 = 2\alpha D^2\left(\frac{2\pi kT}{\mu}\right)^{\frac{1}{2}} e^{-\epsilon^*/kT} \sum_{r=0}^{s} \frac{1}{r!}\left(\frac{\epsilon^*}{kT}\right)^r. \qquad (1205, 15)$$

Provided $\epsilon^* \gg skT$ (the condition $\epsilon^* \gg kT$ is insufficient) we may replace (15) by the approximation

$$k_2 \simeq 2\alpha D^2\left(\frac{2\pi kT}{\mu}\right)^{\frac{1}{2}} \frac{1}{s!}\left(\frac{\epsilon^*}{kT}\right)^{s} e^{-\epsilon^*/kT}, \qquad (1205, 16)$$

which is also of the form (11) with $Q = \epsilon^*$ and $r = -(s-\frac{1}{2})$.

In this discussion we have tacitly ignored rotational degrees of freedom. It is possible that these may also contribute to $\epsilon^*$. In a simple collision between two non-linear molecules there are six rotational degrees of freedom altogether. But owing to the conservation of angular momentum only three could contribute to $\epsilon^*$ without restriction. If this happens the number of squared terms contributing to $\epsilon^*$ will be odd and the formulae of this section should be revised. It does not, however, seem worth while doing this, since we have already used the crude approximation of treating each vibrational freedom contributing to $\epsilon^*$ as completely classical and consequently $s$ is in any case an ill-defined number.

**§ 1206. Simple collision theories.** We have so far left unspecified the number $s$ of classical internal vibrations contributing to $k_2$. The simplest possible assumption is that none of them contribute. The formulae of the preceding section then simplify as follows.

*First simple collision theory.* If we assume that $\kappa$ the probability of reaction is equal to a constant $\alpha$ when the *total* relative translational energy

has a specified value greater than $\epsilon^*$ and is otherwise zero, we obtain in place of (1205, 13)

$$k_2 = 2\alpha D^2\left(\frac{2\pi kT}{\mu}\right)^{\frac{1}{2}}\left(\frac{\epsilon^*}{kT}+1\right)e^{-\epsilon^*/kT}. \qquad (1206, 1)$$

If $\epsilon^* \gg kT$ we may replace this by the approximation

$$k_2 \simeq 2\alpha D^2\left(\frac{2\pi kT}{\mu}\right)^{\frac{1}{2}}\frac{\epsilon^*}{kT}e^{-\epsilon^*/kT}, \qquad (1206, 2)$$

of the form (1205, 11) with $Q = \epsilon^*$ and $r = -\frac{1}{2}$. For the temperature coefficient of $k_2$ we deduce

$$kT^2\frac{\partial \log k_2}{\partial T} = \epsilon^* + kT\left(\frac{1}{2} - \frac{1}{kT/\epsilon^*+1}\right), \qquad (1206, 3)$$

or provided $\epsilon^* \gg kT$

$$kT^2\frac{\partial \log k_2}{\partial T} \simeq \epsilon^* - \tfrac{1}{2}kT. \qquad (1206, 4)$$

*Second simple collision theory.* If we assume alternatively that $\kappa$, the probability of reaction, is equal to a constant $\alpha$ when the relative translational energy *along the line of centres* exceeds a specified value $\epsilon^*$, and is otherwise zero, then we obtain in place of (1205, 15)

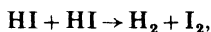
$$k_2 = 2\alpha D^2\left(\frac{2\pi kT}{\mu}\right)^{\frac{1}{2}}e^{-\epsilon^*/kT}, \qquad (1206, 5)$$

which is of the form (1205, 11) with $r = \frac{1}{2}$, or in other words of the form (1205, 12). For the temperature coefficient of $k_2$ we deduce

$$kT^2\frac{\partial \log k_2}{\partial T} = \epsilon^* + \tfrac{1}{2}kT. \qquad (1206, 6)$$

**§ 1207. Comparison of simple collision theories with experiment.** To compare either of the simple collision theories with experiment one requires measurements of the rate constant over a range of temperatures. The temperature coefficient determines $\epsilon^*$ by (1206, 4) or (1206, 6), according to which of the two theories we wish to compare with experiment. The absolute values of the rate constants then give experimental values for the product $\alpha D^2$. The product $\alpha\pi D^2$ may be regarded as the effective target area for a reactive collision, and neither of the factors $\alpha$ and $\pi D^2$ is precisely defined alone. There is, however, some virtue in not amalgamating them. One can suppose ideally that $\pi D^2$ has been determined approximately by viscosity measurements, when it will have the physical meaning of the effective target area for momentum exchange in an encounter. By using this value for $\pi D^2$ we can obtain a value for $\alpha$.

Let us take the specific example

$$HI + HI \rightarrow H_2 + I_2,$$

studied in detail by Bodenstein and again recently by Kistiakowsky, and shown to be homogeneous and of second order from 550° K. to 789° K.† Over this range the rate can within the experimental accuracy be expressed empirically by any of the formulae

$$k_2 = 8 \times 10^{-11} e^{-22{,}000/T} \text{ cm.}^3/\text{molecule sec.,} \qquad (1207, 1)$$

$$k_2 = 2 \times 10^{-9} T^{-\frac{1}{2}} e^{-22{,}000/T} \text{ cm.}^3/\text{molecule sec.,} \qquad (1207, 2)$$

$$k_2 = 3 \times 10^{-12} T^{\frac{1}{2}} e^{-22{,}000/T} \text{ cm.}^3/\text{molecule sec.,} \qquad (1207, 3)$$

so that we may take $\epsilon^*/k = 22{,}000$ deg. In the experimental temperature range $\epsilon^*/kT \simeq 22{,}000/700 \simeq 30$, so that we may use the approximate formulae valid for $\epsilon^* \gg kT$. If we insert the numerical values $\epsilon^*/k = 22{,}000$ deg., $\mu = \frac{1}{2} \times 128 \times 1{\cdot}65 \times 10^{-24}$ g., and $D = 3{\cdot}5 \times 10^{-8}$ cm. into formulae (1206, 2) and (1206, 5) in turn, we obtain

$$k_2 = 1{\cdot}5 \times 10^{-7} \alpha T^{-\frac{1}{2}} e^{-22{,}000/T} \text{ cm.}^3/\text{molecule sec.,} \qquad (1207, 4)$$

$$k_2 = 7 \times 10^{-12} \alpha T^{\frac{1}{2}} e^{-22{,}000/T} \text{ cm.}^3/\text{molecule sec.} \qquad (1207, 5)$$

By comparison of (4) with (2) we find that the first theory leads to $\alpha \simeq 1/75$, while by comparison of (5) with (3) we find that the second theory leads to $\alpha \simeq 0{\cdot}5$

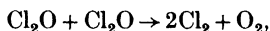
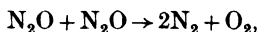
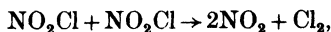
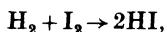
The exact value assumed for $D$ will of course affect the values found for $\alpha$, but will not alter their order of magnitude. By choosing for $D$ the value $2{\cdot}5 \times 10^{-8}$ cm, we can make the value of $\alpha$ given by the second theory exactly unity. It is not possible to decide whether $\alpha$ is actually unity or merely of the order of magnitude unity, but it is certainly striking that the absolute value of the rate can be calculated at least within a factor of about 3 by using the second theory, and the value of $\pi D^2$ deduced from viscosity measurements for $\alpha\pi D^2$. This agreement has led to the following tentative theory *those collisions and only those collisions lead to reaction, in which the relative translational energy along the line of centres exceeds a specified value* $\epsilon^*$ *called the activation energy*. This theory leads to the formula

$$k_2 = 2D^2\left(\frac{2\pi kT}{\mu}\right)^{\frac{1}{2}} e^{-\epsilon^*/kT}. \qquad (1207, 6)$$

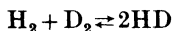
To test this theory for other reactions, one determines the activation energy $\epsilon^*$ from the temperature coefficient of $k_2$, and then from the absolute value of $k_2$ one calculates the value of $D$ which fits formula (6). If the value found for $D$ is of the order of a few Ångströms, the theory is at least not impossible. For reactions between two complicated molecules it will probably be necessary for the right parts of the two molecules to come into contact, and consequently such molecules should have an effective collision

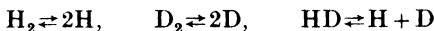
† For detailed references see Hinshelwood, *The Kinetics of Chemical Change in Gaseous Systems*, Ed. 3 (Oxford, 1933).

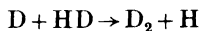
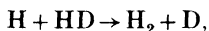
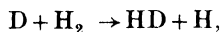
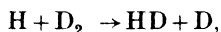
diameter $D$ no greater than smaller and simpler molecules have. The theory has been tested in this way by Hinshelwood* for the reactions

$$H_2 + I_2 \rightarrow 2HI, \qquad NO_2Cl + NO_2Cl \rightarrow 2NO_2 + Cl_2,$$
$$N_2O + N_2O \rightarrow 2N_2 + O_2, \qquad C_2H_4 + H_2 \rightarrow C_2H_6;$$
$$Cl_2O + Cl_2O \rightarrow 2Cl_2 + O_2,$$

in every case agreement is obtainable with formula (6) with a value of $D$ of the order of a few Ångströms. All the above-mentioned reactions are bimolecular and second order.

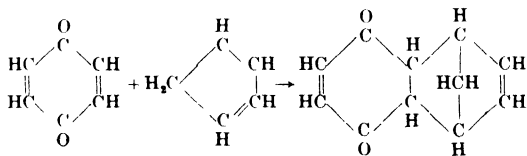
The stoichiometric reactions such as

$$H_2 + D_2 \rightleftarrows 2HD$$

are of the order $\frac{3}{2}$, and can be explained by assuming that the equilibria

$$H_2 \rightleftarrows 2H, \qquad D_2 \rightleftarrows 2D, \qquad HD \rightleftarrows H + D$$

are exactly maintained, while the bimolecular processes

$$H + D_2 \rightarrow HD + D, \qquad D + H_2 \rightarrow HD + H,$$
$$H + HD \rightarrow H_2 + D, \qquad D + HD \rightarrow D_2 + H$$

are slow and determine the rates. The rates of these bimolecular processes can be deduced from the experimental data of Farkas and Farkas,† and they too are in agreement with formula (6), with an assumed value of $1{\cdot}2 \times 10^{-8}$ cm. for $D$. It thus appears that this very simple theory leads to absolute values of the rate correct to within a factor of about 3. Since empirically, if the theory were wrong, one might obtain values of $D$ wrong by many powers of 10, the test is quite a severe one.

It is perhaps worth mentioning that there are reactions for which values of $D$ of a few Ångström units lead to a value of $\alpha$ small compared with unity, usually about $10^{-5}$, but the reason is obvious as will be clear from an example. The reaction

```
       O                H                    O       H
       C              C                    C   H   C
  HC      CH        /   CH          HC      C    |   CH
  ||      ||   + H2C     |     →    ||      |   HCH  ||
  HC      CH        \\  CH          HC      C    |   CH
       C              C                    C   H   C
       O              H                    O       H
```

and several similar reactions have been studied,‡ and give values of $\alpha$ of the order $10^{-5}$. These reactions are examples of ring closure, in which a new ring is formed, and it is obvious that for reaction to occur the two reacting molecules must make contact at two distinct specified places. This geo-

* Hinshelwood, *loc. cit.* p. 489. † Farkas and Farkas, *Proc. Roy. Soc.* A, **152**, 124 (1935).
‡ See Wassermann, *Trans Fara. Soc.* **34**, 128 (1938).

metrical requirement is sufficient to account for the extra factor. Such exceptional cases do not affect the usefulness of the simple theory for simple reactions.

**§ 1208. A refined formulation of bimolecular reaction rates.** It has recently been shown by Eyring and others* that a reformulation of bimolecular reaction rates can be made, which depends on equilibrium theory to just the same extent as the previous formulation in terms of collisions, but which goes deeper and is more illuminating than the older formulation. At present the results obtainable by the two treatments are much the same, but the newer treatment should prove more useful in the future for the *a priori* calculation of reaction rates from purely atomic data.

The ideas underlying the new formulation are as follows. The forces between the atoms of the molecules in reaction are due to the motion and distribution of their electrons and the charges on their own nuclei. These forces can in principle be calculated by quantum theory, and even in the most violent collisions, at least for many reactions, the relative motions of the nuclei are slow and the forces are those corresponding to the same static configuration of the nuclei. This means of course that we may assume that the action is quasi-static, and that no electronic transitions occur with any appreciable probability. In the configuration space of the reacting complex we can therefore set up a potential energy function, which defines the configurational energy of the complex at every stage of any collision. In this potential energy field the relative motion of the various nuclei must be treated by quantum theory when necessary; there may be vibrations of too high a frequency for a classical approximation, but in general all tunnelling effects may be neglected, and the treatment of the nuclear states of motion may at least be taken to be quasi-classical. It is, however, a definite assumption that the potential energy function is unique, and that no electronic transitions occur. When such transitions occur reaction rates of a different order of magnitude may be found. We shall not consider such reactions here. If the number of atoms concerned in any reaction is $q$, $q$ is at least 3, and the configuration space is of $3q$ dimensions. But since the position of the centre of mass of the complex is irrelevant, and since the potential energy function is also independent of the rotation of the complex as a whole, the configuration space required for the representation of the potential energy function, and the essential details of the relative motion, reduces to $3q-6$ dimensions, or $3q-5$ if the complex is linear.

Let us now consider the nature of the potential energy function more

* See for example Eyring, *J. Chem. Phys.* **3**, 107 (1935); Hirschfelder, Eyring and Topley, *J. Chem. Phys.* **4**, 170 (1936), where further references will be found.

closely. For certain configurations the potential energy will be low. These regions correspond to the separation of the reactants or products to great distances. These regions will be separated by a potential energy mountain range, and, owing to the factor $e^{-\epsilon/kT}$ affecting the probability of occurrence of any configuration, the lowest pass in this range will be the route by which the reaction occurs. When the combined pair of reactants is in a configuration near the pass, and in a state of motion in which its representative point in configuration space can cross the pass, the combined pair may be called *an activated complex.* The calculation of reaction rates by application of equilibrium theory proceeds by calculating the equilibrium number of activated complexes present in the gas at any temperature, and the rate at which any activated complex gives rise to an effective reaction. The method will be explained more precisely in a moment. The whole method is therefore still based on the assumption that the reaction rate is not fast enough to upset the equilibrium calculation of the number of activated complexes. This assumption is just as essential a part of the refined theory as it was of the cruder collision theory.

The lowest pass mentioned above may be a simple pass, but need not be so. If it is not simple, it leads first from the region of separated reactants to a limited high level basin in configuration space, points in which correspond to the formation of an *associated complex.* There must then be a second lowest pass in the rim of the high level basin leading from the basin to the region of separated products. When there is no high level basin, the rate of reaction is merely the rate at which activated complexes reach the pass in such a direction that (regarded as classical particles) they can pass over and through it. When there is a high level basin, then this rate is merely the rate of entry to the basin, and the rate of reaction is this rate of entry multiplied by the probability that the associated complex breaks down by exit over the second pass and not by return over the pass of entry.

It is now possible to give the equilibrium calculation of the number of activated complexes, and hence the rate at which the representative points of the complexes cross the pass of entry, for a volume $V$ of the reacting gas in which there are $N_1$ and $N_2$ molecules of the two reactants respectively. Every pair of molecules $(1, 2)$ is a complex for which the complete partition function to a sufficient approximation is $f_1(T)\, f_2(T)$, the separate factors being the usual partition functions for the two reactants. There are $N_1 N_2/\sigma_{12}$ such complexes in all. We now require the fraction of such complexes which are activated, that is to say the fraction in the neck of the pass, whose position and momentum in a suitable coordinate $x^*$ corresponding to motion across the pass lie in the range $dx^* dp_x^*$, all other coordinates and momenta having any values whatever consistent with these. This fraction

will be calculable, if we can construct the partial partition function for such activated configurations. Let us now consider the nature of the potential energy for the complex in this region. By definition of the pass the potential energy in this region will be a minimum for variations of any other configurational coordinate, except the special one corresponding to passage across the range, for which it is a maximum. We shall assume this maximum to be so flat that motion across the pass is practically a free translation. We can therefore set up a partition function for the activated complex by integrating or summing over all types of motion of the complex in the other variables, consistent with the specified values of $x^*$ and $p_x^*$, thus constructing a quasi partition function $f_\tau(T)$ in $3q-1$ configurational variables and their corresponding momenta, and multiplying it by the partition function corresponding to the possession of the specified values of $x^*$ and $p_x^*$ themselves. This latter factor is

$$e^{-\epsilon^*/kT}\,dx^*\,dp_x^*/h,$$

where $\epsilon^*$ is the energy in this coordinate, which must satisfy $\epsilon^* \geqslant \epsilon_0$, $\epsilon_0$ being the height of the pass. The equilibrium number of these activated complexes is therefore

$$\frac{N_1 N_2}{\sigma_{12}}\frac{f_\tau(T)}{f_1(T)f_2(T)}e^{-\epsilon^*/kT}\frac{dx^*\,dp_x^*}{h}. \qquad (1208, 1)$$

The energy zero for the calculation of $f_\tau(T)$ is now taken at the top of the pass.

Representative points corresponding to these activated complexes cross the pass at a rate obtained by replacing $dx^*$ in (1) by $p_x^*/\mu^*$; for if $\mu^*$ is the effective mass of the complex for relative motion in this coordinate, $p_x^*/\mu^*$ is then the velocity of approach of the representative point to the pass. The total number of crossings of the pass in unit time in volume $V$ is therefore

$$\frac{N_1 N_2}{\sigma_{12}}\frac{f_\tau(T)}{f_1(T)f_2(T)}\int_{\epsilon_0}^{\infty} e^{-\epsilon^*/kT}\frac{p_x^*\,dp_x}{\mu^* h}. \qquad (1208, 2)$$

If, as will usually be accurate enough, we put

$$\epsilon^* = \epsilon_0 + \tfrac{1}{2}p_x^{*2}/\mu^*, \qquad (1208, 3)$$

where $\epsilon_0$ is the height of the pass, then this rate of crossing reduces to

$$\frac{N_1 N_2}{\sigma_{12}}\frac{f_\tau(T)}{f_1(T)f_2(T)}\frac{kT}{h}e^{-\epsilon_0/kT}. \qquad (1208, 4)$$

If $\kappa$ is the fraction of these crossings which result in reaction, then the number of reactions taking place per unit volume and per unit time is

$$\kappa\frac{N_1 N_2}{V}\frac{f_\tau(T)}{f_1(T)f_2(T)}\frac{kT}{h}e^{-\epsilon_0/kT}. \qquad (1208, 5)$$

In omitting $\sigma_{12}$ we have assumed that if the two molecules 1 and 2 are of the same type they are both destroyed by the reaction. If we introduce $\phi(T)$ to denote a partition function with the volume factor removed, so that

$$f(T) = V\phi(T), \tag{1208, 6}$$

we obtain for the second order rate constant $k_2$

$$k_2 = \kappa \frac{\phi_\tau(T)}{\phi_1(T)\,\phi_2(T)} \frac{kT}{h} e^{-\epsilon_0/kT}. \tag{1208, 7}$$

In certain simple reactions $\kappa$ may be assumed to be unity, or at least a fraction of the order of magnitude of unity, and the usefulness of the method then depends on ability to evaluate $\phi_\tau(T)$.

Without going into details for any particular reaction the general nature of the factors in $\phi_\tau(T)$ can be made evident. From the potential energy function in $3q-5$ or $3q-6$ variables, assumed known, the configuration of the atoms when the representative point is in the neck of the pass can be derived. This configuration being fixed, the complex as a whole has a mass $(m_1+m_2)$ and its translational motion will contribute to $\phi_\tau(T)$ a factor

$$\lambda_\tau(T) = (2\pi[m_1+m_2]\,kT)^{\frac{3}{2}}/h^3. \tag{1208, 8}$$

The complex is also free to rotate as a whole. This rotation will contribute to $\phi_\tau(T)$ the factor

$$r_\tau(T)/\sigma_\tau = 8\pi^2 A_\tau kT/\sigma_\tau h^2 \tag{1208, 9}$$

if the configuration is linear, and the factor

$$r_\tau(T)/\sigma_\tau = 8\pi^2(2\pi kT)^{\frac{3}{2}}\,(A_\tau B_\tau C_\tau)^{\frac{1}{2}}/\sigma_\tau h^3 \tag{1208, 10}$$

if the configuration is non-linear; $A_\tau$, $B_\tau$ $C_\tau$ denote moments of inertia, and $\sigma_\tau$ the symmetry number of the complex. The coordinates $x^*, p_x^*$ have already been allowed for. The configuration is stable in the remaining $3q-6$ or $3q-7$ freedoms, and they may be taken each to supply a normal mode of definite frequency with a corresponding vibrational factor in $\phi_\tau(T)$, completely determined by the potential energy surface. In this way $\phi_\tau(T)$ may be formally constructed, and the reaction rate (7) calculated *a priori*, so far as equilibrium considerations allow.

**§ 1209. Relationship of the refined theory to the simple collision theory.** It is instructive to compare the calculation of a reaction rate by the refined theory and by the simple collision theory in the simplest possible case, and then to see how the difficulties increase as we pass from the simplest to the more complex cases.† The simplest conceivable case is the union of

† This discussion is based on Hinshelwood, *J. Chem. Soc.* p. 635 (1937). Compare also Eyring, *J. Chem. Phys.* 3, 114 (1935).

two atoms of different types 1 and 2. Actually this is not a type of collision that leads to reaction, as it possesses no means of getting rid of the excess internal energy of the molecule so formed. This means that in practice $\kappa$ would be zero or nearly zero. Nevertheless this practical limitation does not affect the suitability of the example for illustrative purposes. For the free atoms of masses $m_1$ and $m_2$ we have the partition functions, with the volume factor omitted

$$\phi_1(T) = (2\pi m_1 kT)^{\frac{3}{2}}/h^3, \tag{1209, 1}$$

$$\phi_2(T) = (2\pi m_2 kT)^{\frac{3}{2}}/h^3. \tag{1209, 2}$$

The activated complex in this simple case resembles a diatomic molecule in having only two rotational degrees of freedom, and no other internal degrees of freedom apart from the reaction coordinate which may be taken as the distance between the two atoms. Hence the quasi partition function of the activated complex for all degrees of freedom other than that of the reaction coordinate and with the volume factor removed is

$$\phi_\tau = \frac{(2\pi[m_1+m_2]\,kT)^{\frac{3}{2}}}{h^3}\,\frac{8\pi^2 A\,kT}{h^2}. \tag{1209, 3}$$

Here $A$ denotes the principal moment of inertia of the activated complex and the energy zero is taken at the top of the pass. Substituting (1), (2) and (3) into (1208, 7), we obtain for the rate constant

$$k_2 = \kappa\,\frac{(2\pi[m_1+m_2]\,kT)^{\frac{3}{2}}\,(8\pi^2 A\,kT)}{(2\pi m_1 kT)^{\frac{3}{2}}\,(2\pi m_2 kT)^{\frac{3}{2}}}\,kT\,e^{-\epsilon_0/kT}, \tag{1209, 4}$$

the $h$'s cancelling. Let us now redefine the collision diameter $D$ as the distance apart of the two atomic nuclei in the neck of the pass, so that

$$A = \frac{m_1 m_2}{m_1+m_2}\,D^2. \tag{1209, 5}$$

Substituting (5) into (4), and introducing the reduced mass

$$\mu = m_1 m_2/(m_1+m_2),$$

we obtain

$$k_2 = \kappa 2D^2\left(\frac{2\pi kT}{\mu}\right)^{\frac{1}{2}} e^{-\epsilon_0/kT}, \tag{1209, 6}$$

which is of exactly the same form as (1206, 5), if we identify $\epsilon_0$, the energy at the top of the pass, with $\epsilon^*$, the minimum relative translational energy required for reaction in the simple collision theory, and $\alpha$ with $\kappa$. For this very simple case of reaction between two atoms we see then that the refined theory is exactly equivalent to the second simple collision theory. The collision diameter in the latter theory is the distance apart of the nuclei in the neck of the pass of the former theory. A probability coefficient $\kappa$ or $\alpha$

occurs in an exactly similar way in both theories, and in both its value has to be estimated to lead to definite results.

As soon as we pass over to actual bimolecular reactions more than two atoms are involved, and the activated complex has other degrees of freedom, most of them vibrational. One then has two alternatives. Either one assumes that the partition functions for these vibrational degrees of freedom just cancel the vibrational partition functions of the free reacting molecules; the theory then reduces to a paraphrase of the simple collision theory and leads no further than the latter. The other alternative is to determine the structure and so the normal modes of the activated complex. This is a problem in pure quantum theory. Like most such problems it is in principle soluble, but in practice insoluble except by making drastic approximations. We shall review very briefly the attacks that have been made in this direction.

**§ 1210. Application of refined theory.** The problem of determining *a priori* the structure, and in particular the energy, of the activated complex was first attacked by London,* who indicated how for a very simple process a crude solution could be obtained by rather drastic approximations. His method was developed by Pelzer and Wigner.† The approximations used have been analysed and severely criticized by Coolidge and James,‡ and the formulae dependent on them must be regarded as semi-empirical. Such formulae have been used by Polanyi, Eyring and others.§ The extent of their usefulness is admirably assessed in a paper by Hirschfelder, Eyring and Topley.‖ The position can be summed up as follows: Not even for the simplest bimolecular process is it possible to calculate the interaction between two molecules with an accuracy adequate to give even a useful approximation to the energy of activation. If, however, the empirical value of the energy of activation is assumed, it is possible for the very simplest processes between an atom and a diatomic molecule to obtain a useful semi-quantitative estimate of the interaction energy for all important relative configurations and in particular for the activated complex. When we remember the immense labour required to calculate the interaction of even two H atoms to form an $H_2$ molecule, there seems little hope in the near future of computing the interaction between two molecules or between

* London, *Probleme der Modernen Physik*, p. 104 (Sommerfeld-Festschrift, Leipzig, 1928).

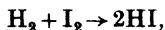
† Pelzer and Wigner, *Zeit. Physikal. Chem.* B, **15**, 445 (1932); Wigner, *Zeit. Physikal. Chem.* B, **19**, 203 (1932).

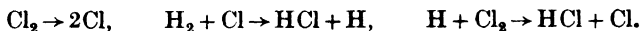
‡ Coolidge and James, *J. Chem. Phys.* **2**, 811 (1934).

§ Eyring and Polanyi, *Zeit. Physikal. Chem.* B, **12**, 279 (1931); Eyring, *J. Am. Chem. Soc.* **53**, 2537 (1931); Farkas and Wigner, *Trans. Fara Soc.* **32**, 708 (1936); Hirschfelder, Eyring and Topley, *J. Chem. Phys.* **4**, 170 (1936).

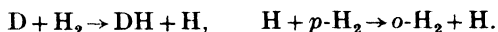
‖ Hirschfelder, Eyring and Topley, *J. Chem. Phys.* **4**, 170 (1936), first two pages.

a molecule and an atom with sufficient accuracy to be useful. The real interest of calculations of this type is that they lead to a qualitative picture of the part of phase space corresponding to the activated complex. Probably the most striking achievement of these semi-quantitative computations is their use by Eyring* to obtain values of energies of activation, which while extremely rough are nevertheless adequate to explain why the reaction between hydrogen and iodine proceeds by the mechanism

$$H_2 + I_2 \rightarrow 2HI,$$

whereas that between hydrogen and chlorine proceeds by the mechanisms

$$Cl_2 \rightarrow 2Cl, \qquad H_2 + Cl \rightarrow HCl + H, \qquad H + Cl_2 \rightarrow HCl + Cl.$$

The calculations are insufficiently accurate to predict without ambiguity which will be the mechanism for the reaction between hydrogen and bromine, but indicate that it may well involve bromine atoms, as in fact it does.

Whereas, owing to the mathematical complexity of the problem, it is not yet possible to determine the configuration of the activated complex with sufficient accuracy to predict the activation energy, it is, however, possible by taking the experimental value of the activation energy to deduce at least plausible configurations in phase space for the path traversed by a pair of molecules when they react. Considerable progress in this direction has been made in the processes of the type

$$D + H_2 \rightarrow DH + H, \qquad H + p\text{-}H_2 \rightarrow o\text{-}H_2 + H.$$

We shall describe briefly the results obtained by Hirschfelder, Eyring and Topley† for processes of this type. All the reaction rates observed can be successfully interpreted in terms of a single semi-empirical potential energy surface. For the reactants $H_2 + H$ (or the corresponding sets in which any number of H's are replaced by D's) the activated complex is linear. The potential energy can therefore be represented in a configuration space of $3 \times 3 - 5 = 4$ variables, but the representation is simplified by the symmetry of the surface. If the distance apart of the H nuclei is fixed at any value, then the equipotential surfaces are surfaces of revolution about the line of the H nuclei. Fig. 1 shows a section of them when two H nuclei are fixed at their ordinary equilibrium separation. These curves, combined with the curves of Fig. 2 showing the equipotential surfaces for the straight configuration and variable nuclear distances, are sufficient to enable all the features essential to the calculation of reaction rates to be deduced.

* Eyring, *J. Am. Chem. Soc.* **53**, 2537 (1931).

† Hirschfelder, Eyring and Topley, *J. Chem. Phys.* **4**, 170 (1936).

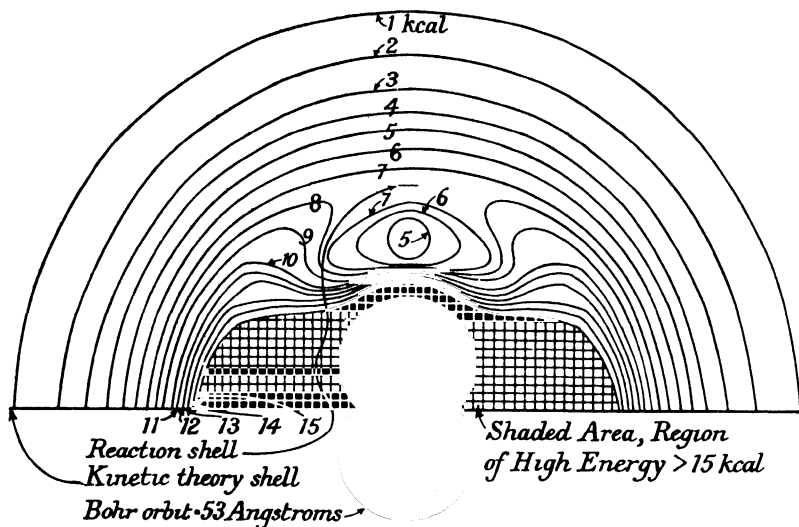



Fig 1 Showing a set of equipotential surfaces for the three atoms in the complex $H_2 + H$ when the nuclear separation of two H atoms is fixed at its normal value in $H_2$ (Energies in Kcal /mole )

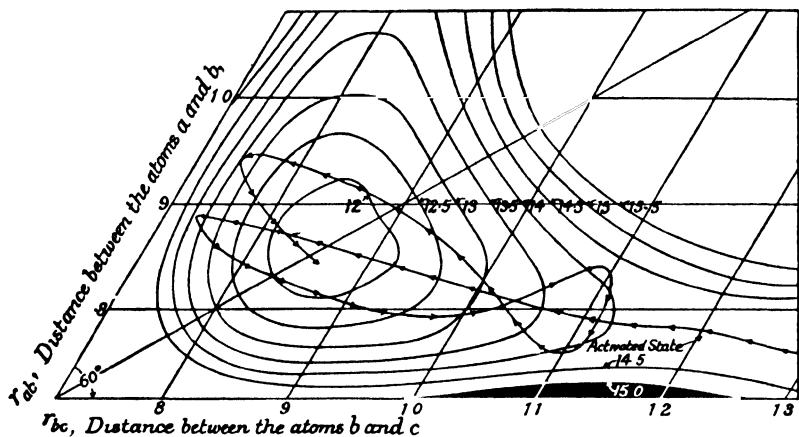
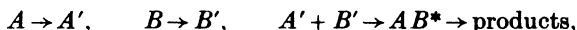



Fig 2 Showing equipotential surfaces for the linear configurations of $H_2 + H$ as functions of the two internuclear distances $r_{ab}$ and $r_{bc}$ The motion of the representative point for a linear vibrational disturbance of the complex is shown (Energies in Kcal /mole , distances in Å )

The trajectory shown in Fig. 2 is of some importance. Its considerable complication, combined with the fact that the passes of entry and exit to the high level basin are in this case of identical level and form, shows that we may safely assume that exit from either is equally likely. Thus for any reaction of the form $H_2 + D \rightarrow HD + H$, $\kappa \simeq \frac{1}{2}$. This estimate must be modified when the passes are different, or the activated complex has a different residual energy in the two passes—refinements which we shall not pause to describe. For the ortho $\rightarrow$ para transformation by $H_2 + H \rightarrow H + H_2$ however, we must take $\kappa = \frac{1}{8}$, or for para $\rightarrow$ ortho $\kappa = \frac{3}{8}$; the conversion can only occur if the representative point emerges from the other pass than that of entry, and even if it does so, at these temperatures ortho and para molecules will be formed in the ratio 3 : 1.

**§ 1211. Applicability of equilibrium theory to bimolecular processes.** For two molecules $A$ and $B$ to react according to the bimolecular mechanism, they have to pass through the stages

$$A \rightarrow A', \qquad B \rightarrow B', \qquad A' + B' \rightarrow AB^* \rightarrow \text{products},$$

where $A'$, $B'$ denote molecules with sufficient excess energy above that of average molecules for the formation of a reacting complex $AB^*$. According to the crude collision theory, the formation of $AB^*$ from $A'$ and $B'$ is determined by the single condition that $A'$ and $B'$ should meet with sufficient relative kinetic energy in the direction of the line of centres. According to a more general formulation due to Marcelin†, the reacting complex $AB^*$ is defined by the condition that the representative point in phase space should cross a certain critical surface. Eyring's formulation improves on Marcelin's only in its inclusion of a formal description of the part of phase space corresponding to the reacting complex. In all three formulations the rate of the reaction is determined by the formation of $AB^*$ from $A'$ and $B'$. In all three formulations it is justifiably assumed that the rate of formation of $AB^*$ from $A'$ and $B'$ is given in terms of the concentrations of $A'$ and $B'$ by the formula which holds for complete equilibrium. What is required is, however, a formula for the rate of formation of $AB^*$ in terms of the concentrations of average molecules $A$ and $B$. To obtain this it is further assumed in all three formulations that the concentrations of energetic molecules $A'$, $B'$ are related to the concentrations of average molecules, $A$, $B$ by the formula for complete equilibrium. It is important to realize that this is an additional assumption common to all versions which apply equilibrium theory to calculate the rate of reaction. It is apparently sometimes assumed

† Marcelin, *Ann. Physique*, 3, 158 (1915).

without justification that this condition is obviously fulfilled. In other cases there appears to be some confusion between the two distinct questions:

(*a*) Is the formation of $AB^*$ from $A'$ and $B'$ governed by the same law as under equilibrium conditions?

(*b*) Are the concentrations of $A'$, $B'$ related to those of $A$, $B$ by the equilibrium formulae?

It is the latter assumption that is difficult to justify theoretically. The energetic molecules $A'$, $B'$ can be formed from average molecules $A$, $B$ only by a series of fortuitously propitious collisions with other molecules or by collision with the wall. Whether the concentrations of $A'$, $B'$ are maintained effectively at their equilibrium concentrations relative to those of $A$, $B$ depends entirely on the efficiency of the collision mechanism. The strongest evidence, that the supply of energetic molecules is, in fact, maintained, is the success of the crude collision theory, but this is *a posteriori* evidence. To establish the validity of the assumption on theoretical grounds would require a detailed consideration of the effectiveness of collisions in producing energetic molecules. Up to the present such a calculation has proved intractable, and we shall try to indicate the difficulties it meets with, by further discussion of the simplest case in which the molecules $A$, $B$ are of equal mass and no important excitation of internal vibrations need be considered.

It can be shown that, in order that the energetic molecules may be maintained at their equilibrium concentration, it is necessary and sufficient that the number of energetic molecules reacting in unit time shall be a small fraction of the number of energetic molecules reduced to normal by ordinary collisions. It is hardly necessary to set out the argument formally. For the equilibrium relations between the energetic molecules $A'$, $B'$, and the normal molecules $A$, $B$ are maintained by a balance of the rates of creation and destruction of the $A'$, $B'$ molecules by collisions, and if the rate of destruction is only slightly altered by the introduction of a new lethal process, the new equilibrium concentrations of $A'$ and $B'$ will only fall slightly below the old values before a new balance is set up. Now the reaction rates can, as we have seen, be successfully calculated by assuming that reaction occurs whenever the head-on relative velocity of the pair of molecules along the line of centres corresponds to an energy which is a rather large multiple of $kT$. Such collisions if not reactive would, apart from conversion of relative kinetic energy into vibrational energy, merely reverse the head-on relative velocity. This reversal redistributes the total kinetic energy between $A'$ and $B'$, in a manner which depends on the relative directions of the relative velocity and the velocity of the centre of mass of the pair. Such a redistribution will generally reduce the kinetic energy of the more energetic mole-

cule of the pair, and thus reduce the number of energetic molecules, but it will not always do this. There are, however, a large number of other collisions of type $A'$, $B'$, in which the head-on relative velocity has lower values, so that no reaction will occur on this theory. We cannot, however, be sure that a large number of these collisions will normalize the more active molecule, for again all the collisions can do is to reverse the head-on component of the relative velocity; and when this component is small the collision is ineffective. This feature of the persistence of a high velocity in a single molecule over several collisions is well known in other branches of kinetic theory. It may well be that the reactive collisions are actually a small fraction of all the normalizing collisions, but the most that can fairly be claimed in this simple way is that this fraction is definitely less than unity and possibly, though not certainly, small. This conclusion is not really as unsatisfactory as it appears at first sight. For it assures us that, though the usual calculations do not certainly yield a rigorous formula for the reaction rate, they will be most unlikely to be in error by more than a numerical factor of the order of 2 or 3, which is of the order of the uncertainty in the other factors such as the collision diameter used in the calculation.

The best independent check on this conclusion is provided by the classical theory of transport phenomena in gases, where a very similar situation arises; in this problem, however, both an approximate solution, similar to that used here, and the exact solution are known. If one attempts to calculate the viscosity and thermal conductivity of a gas by assuming that the distribution laws are everywhere locally those of the equilibrium state, merely altered by local variations of mass motion or temperature, one finds results that may be in error at times by factors of the order 2 or 3. These factors here are accurately known because the approximate equilibrium solution of the problem can be compared with the exact result of solving Boltzmann's integro-differential equation* for the non-equilibrium distribution law, set up in each volume element by the balance between the effects of molecular collisions there, which attempt to restore the usual form, and the distorting effects of molecules arriving from other volume elements in which the regime is different.

**§ 1212. Unimolecular processes.** The existence of unimolecular processes remained for many years a puzzle. Its solution was given independently and almost simultaneously by Christiansen and by Lindemann.† According to this theory an isolated molecule $A$ with average energy cannot

* For example· Chapman, *Phil Trans Roy. Soc* **211**, 433 (1911); **216**, 279 (1916), **217**, 115 (1917)

† Christiansen, *Reaktionskinetiske Studier* (Copenhagen, August 1921), pp. 50–51 Lindemann. *Trans. Fara Soc.* **17**, 599 (1922).

react, but an active molecule, that is a molecule with more than a certain specified amount of energy distributed over a number of specified internal degrees of freedom, has a definite probability of reacting in unit time, and any such molecule, to be denoted by $A'$, will eventually react *if left long enough undisturbed*. Actually active molecules $A'$ are continually losing their excess energy through collisions, and being reconverted to molecules $A$ with insufficient energy to react, this process being known as *deactivation*. Thus the life of an active molecule can be terminated either by deactivation or by spontaneous decomposition. The resultant order of the reaction rate will depend on the relative probabilities of these two events. If spontaneous decomposition is much less probable than deactivation, then the equilibrium concentration of active molecules will be practically unaffected by the decomposition. This concentration will therefore be proportional to the total concentration and the reaction rate will be first order. If, on the contrary, spontaneous decomposition of an active molecule is much more probable than deactivation by collision, then the rate of reaction will be determined by the rate of production of active molecules and so will be second order. It is easily shown that at sufficiently high pressures the rate will be first order, while at sufficiently low pressures it will be second order.

Let the number of molecules $A$ per unit volume be $\nu$. Let $\lambda_1$ denote the fraction of inert molecules $A$ that are converted in unit time to active molecules $A'$, $\lambda_{-1}$ the fraction of active molecules that are deactivated in unit time, and $\lambda_0$ the fraction of active molecules that spontaneously decompose in unit time. Then provided the number of active molecules is always small compared with the number of inert molecules, a condition always fulfilled in practice, it can be shown that the number of decompositions per unit volume and per unit time is

$$-\frac{\partial \nu}{\partial t} = \nu\lambda_1 \frac{\lambda_0}{\lambda_{-1}+\lambda_0}; \qquad (1212, 1)$$

$\lambda_0$ is a molecular constant, while $\lambda_1$, $\lambda_{-1}$ will depend on the composition and concentrations; for given composition $\lambda_1$, $\lambda_{-1}$ will both be proportional to the concentration or pressure. Hence for sufficiently great pressures (1) reduces to

$$-\frac{\partial \nu}{\partial t} = \nu \frac{\lambda_1}{\lambda_{-1}} \lambda_0 \quad (\lambda_0 \ll \lambda_{-1}). \qquad (1212, 2)$$

But $\lambda_1/\lambda_{-1}$ is independent of the concentration (or pressure) and so (2) represents a first order reaction with rate constant

$$k_1 = \lambda_1 \lambda_0/\lambda_{-1}. \qquad (1212, 3)$$

For sufficiently low pressures on the other hand (1) reduces to

$$-\frac{\partial \nu}{\partial t} = \nu\lambda_1 \quad (\lambda_0 \gg \lambda_{-1}), \qquad (1212, 4)$$

and as $\lambda_1$ is proportional to the concentration this represents a second order rate. The transition from first order to second order rate will occur at pressures such that

$$\lambda_0/\lambda_{-1} \simeq 1. \tag{1212, 5}$$

Under equilibrium conditions the concentration $\nu'$ of active molecules is given by

$$\nu' = \nu\lambda_1/\lambda_{-1}, \tag{1212, 6}$$

since there is no need to distinguish between the concentration of inert molecules and the total concentration of $A$ molecules. If we compare (6) with (3) we see that at sufficiently high pressures for the reaction to be first order the rate constant $k_1$ is equal to the product of $\lambda_0$ and the fraction of molecules that are active. If we assume that the condition that a molecule should be active is that it should have energy exceeding $\epsilon^*$ distributed over $s$ internal vibrations, then according to (1202, 11) the fraction of molecules that are active is

$$e^{-\epsilon^*/kT} \sum_{r=0}^{s-1} \frac{1}{r!}\left(\frac{\epsilon^*}{kT}\right)^r, \tag{1212, 7}$$

and consequently the first order constant is given by

$$k_1 = \lambda_0 e^{-\epsilon^*/kT} \sum_{r=0}^{s-1} \frac{1}{r!}\left(\frac{\epsilon^*}{kT}\right)^r. \tag{1212, 8}$$

If $\epsilon^* \gg skT$ (the condition $\epsilon^* \gg kT$ is insufficient) we may replace (8) by the approximation

$$k_1 \simeq \lambda_0 \frac{1}{(s-1)!}\left(\frac{\epsilon^*}{kT}\right)^{s-1} e^{-\epsilon^*/kT}. \tag{1212, 9}$$

We have assumed that all active molecules have the same probability $\lambda_0$ of decomposing in unit time, whatever their energy (provided it exceeds $\epsilon^*$), and however it be distributed amongst the $s$ specified degrees of freedom. If this is not the case, $\lambda_0$ must be regarded as an average value for all types of active molecules.

§ **1213. Temperature coefficient of unimolecular reactions.** We shall now derive a formula, due to Tolman, for the temperature coefficient of a unimolecular rate constant. The formula is of general validity and can be derived equally readily according to classical theory or according to quantum theory. We shall here give the quantal derivation. Let $\kappa_r$ denote the probability of spontaneous decomposition in unit time of a molecule in the internal state $r$ with an energy $\epsilon_r$. Thus defined, $\kappa_r$ is a molecular property and may depend in an arbitrary manner on the internal state $r$ of the molecule. Now the equilibrium fraction of molecules with this configuration is

$$e^{-\epsilon_r/kT}/\textstyle\sum_r e^{-\epsilon_r/kT}, \tag{1213, 1}$$

degenerate states being counted multiply in the summation. Hence,

assuming the applicability of equilibrium theory, the first order constant $k_1$ for the unimolecular decomposition is obtained by multiplying (1) by $\kappa_r$ and summing over all states. We thus obtain

$$k_1 = \Sigma_r \kappa_r e^{-\epsilon_r/kT} / \Sigma_r e^{-\epsilon_r/kT}. \qquad (1213, 2)$$

If we differentiate (2) logarithmically with respect to $T$, we obtain

$$kT^2 \frac{\partial \log k_1}{\partial T} = \frac{\Sigma_r \epsilon_r \kappa_r e^{-\epsilon_r/kT}}{\Sigma_r \kappa_r e^{-\epsilon_r/kT}} - \frac{\Sigma_r \epsilon_r e^{-\epsilon_r/kT}}{\Sigma_r e^{-\epsilon_r/kT}}. \qquad (1213, 3)$$

But the first term on the right is clearly the average internal energy of all molecules that react in unit time, while the second term is the average internal energy of all molecules. We may therefore express (3) in the form

$$kT^2 \frac{\partial \log k_1}{\partial T} = \text{(Average internal energy of reacting molecules)} - \text{(Average internal energy of all molecules)}. \qquad (1213, 4)$$

This striking result, recalling the analogous (1205, 7) for bimolecular processes, is also due to Tolman,† and in this form is perfectly general.

On the special theory that the condition for a molecule to be active is that it possesses energy exceeding $\epsilon^*$ distributed over $s$ given degrees of freedom and that all such active molecules have the same probability $\lambda_0$ of decomposing spontaneously in unit time, we derived formula (1212, 8) for the rate constant. If we now differentiate this with respect to $T$, we obtain

$$kT^2 \frac{\partial \log k_1}{\partial T} = \epsilon^* - \frac{\sum_{r=1}^{s-1} \frac{kT}{(r-1)!}\left(\frac{\epsilon^*}{kT}\right)^r}{\sum_{r=0}^{s-1} \frac{1}{r!}\left(\frac{\epsilon^*}{kT}\right)^r}. \qquad (1213, 5)$$

Provided $\epsilon^* \gg skT$ (the condition $\epsilon^* \gg kT$ is insufficient), we may replace (5) by the approximation

$$kT^2 \frac{\partial \log k_1}{\partial T} \simeq \epsilon^* - (s-1)kT. \qquad (1213, 6)$$

Comparing this with Tolman's formula (4) and remembering that the average energy of $s$ internal vibrations for all molecules is $skT$, we find that the average energy of all decomposing molecules is approximately $\epsilon^* + kT$, thus exceeding the minimum energy required for decomposition by $kT$.

**§ 1214. The reverse process of unimolecular decompositions.** In order to explain unimolecular reactions we have assumed a mechanism of which one stage consists of the spontaneous explosion of an activated molecule into two or more parts. If the number of such parts is two, then

† Tolman, *J. Am. Chem. Soc.* **42**, 2506 (1920).

the reverse process consists of a collision between two particles leading to a transition which unites them into one. There is no difficulty in supposing that such processes can occur with the necessary frequency for complicated molecules, unlike the case of atomic collisions considered in § 1209. One is tempted to argue that they can practically never occur because the relative kinetic energy will never be adjusted exactly to fit any possible value of the quantized internal energy of the united system, and no third body is concerned in the process to carry away the excess energy. This objection, however, overlooks the fact that, just because the combined system is unstable and able to explode, its levels cannot be perfectly sharp, and the breadths of its levels will exactly enable the reverse recombinations to occur at the proper rate.

**§ 1215. Method of comparison of theory with experiment.** Formula (1212, 8) for the first order rate constant $k_1$ contains three adjustable parameters, $\epsilon^*$, $s$ and $\lambda_0$. We therefore require three pieces of experimental data to determine these. Two such are the temperature coefficient of the rate and the absolute value of the rate. A third is not available as long as the reaction remains first order throughout the experimental pressure range. If, however, by reducing the pressure, one can make the rate decrease and cease to be purely first order, $\lambda_0$ should be of the same order of magnitude as $\lambda_{-1}$ for the pressure range in which this change takes place. Under these circumstances we thus have a method of estimating at least the order of magnitude of $\lambda_0$, provided we are able to calculate $\lambda_{-1}$. Now when an active molecule collides with any other molecule, it is far more likely to lose energy than to gain yet more energy. Moreover, we found in §1213 that the average energy of all molecules that decompose is $\epsilon^* + kT$. It is therefore almost obvious, owing to the exponential factor $e^{-\epsilon^*/kT}$, that the vast majority of active molecules will have an energy between $\epsilon^*$ and $\epsilon^* + 2kT$. We shall find that in all the unimolecular reactions studied $\epsilon^*/kT > 50$. Consequently if an active molecule loses only about 4 % of its energy in a collision, it will usually cease to be active. It follows that the majority of collisions suffered by active molecules are deactivating collisions. Hence we can obtain an estimate of at least the order of magnitude of $\lambda_{-1}$, the probability of deactivation in unit time, by taking the number of collisions suffered by the active molecule in unit time. This will not differ seriously from the average number of collisions in unit time of any molecule. Hence according to (1201, 18) we may set

$$\lambda_{-1} \simeq 2\nu D^2(2\pi kT/\mu)^{\frac{1}{2}} \simeq 2\nu D^2(4\pi kT/m)^{\frac{1}{2}}, \qquad (1215, 1)$$

if all the molecules have the same mass $m$. The symmetry number $\sigma$ occurs

only in the formula for the total number of collisions, but not in the formula for the number of collisions of a given molecule.†

The theory may then be tested as follows. We try to select values for $\epsilon^*$, $s$ and $\lambda_0$ such that the first order rate constant $k_1$ is correctly given by formula (1212, 8) over the whole experimental temperature range, and $\lambda_0$ is approximately equal to $\lambda_{-1}$ given by (1) for that value of the concentration $\nu$ at which the rate ceases to be first order. There are *a priori* no restrictions on the values that may be assigned to $\epsilon^*$ or $\lambda_0$, but the number of classical internal vibrations $s$ postulated must be consistent with the experimental heat capacity of the molecule. Thus the crucial test of the theory is whether one can make formula (1212, 8) fit the experimental facts with a reasonable value for $s$.

**§ 1216. Numerical examples.** We shall now illustrate this method of comparison by a few examples. As we can at the best only hope to fix $s$ correct to about $\pm 1$, while the value of $\lambda_0$ depends on the value assigned to $s$, and as further there is no sharply defined value of $\lambda_0/\lambda_{-1}$ at which the departure from first order rate becomes detectable, we are interested only in the orders of magnitude of $\lambda_0$ and $\lambda_{-1}$. We may therefore with sufficient accuracy provisionally set $D = 10$ Å. $= 10^{-7}$ cm. for all the (large) molecules concerned.

We shall find in all cases that $\epsilon^*/kT > 50$, but in the most unfavourable case $\epsilon^*/skT$ is only about 3, and it is therefore not accurate to assume $\epsilon^* \gg skT$. Nevertheless, as we are here interested only in the order of magnitude of $\lambda_0$, we may still replace (1212, 8) by the approximation

$$k_1 \simeq \lambda_0 \frac{1}{(s-1)!}\left(\frac{\epsilon^*}{kT}\right)^{s-1} e^{-\epsilon^*/kT}, \qquad (1216, 1)$$

as the error introduced will only be a factor of the order 1·5 in the most unfavourable case.

(1) *Decomposition of gaseous diethyl ether.* This reaction‡ proceeds at a convenient rate between 700–860° K., and is homogeneous and first order down to pressures of 200 mm. Hg. Below that pressure of the reactant the reaction proceeds more slowly and approaches the second order type. The final result of the reaction is roughly

$$C_2H_5 . O . C_2H_5 \rightarrow CO + 2CH_4 + \tfrac{1}{2}C_2H_4,$$

though of course this does not represent the primary process which is probably the formation of CO and two unstable hydrocarbons. Sufficient admixture of $H_2$, for example a partial pressure of 300 mm. Hg at 800° K.,

† In *S.M.* the formula at the bottom of p. 701 is wrong by including a factor $\frac{1}{2}$.

‡ References for this and other reactions are given below table 1.

will preserve the unimolecular rate unaltered down to a pressure of 40 mm. Hg of the reactant. He, $N_2$ and the reaction products have no marked effects. The first order rate constant can be represented empirically by

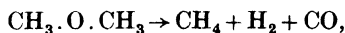
$$k_1 = 3{\cdot}1 \times 10^{11} e^{-26,700/T} \text{ sec.}^{-1},$$

or equally well by

$$k_1 = 6{\cdot}9 \times 10^8 . \frac{1}{3!}\left(\frac{29,000}{T}\right)^3 e^{-29,000/T} \text{ sec.}^{-1},$$

corresponding to the choice $s = 4$ and $\lambda_0 = 6{\cdot}9 \times 10^8 \text{ sec.}^{-1}$. For the number of deactivating collisions per unit time using (1215, 1) and setting* $D = 10^{-7}$, $T = 800$, $m = 74 \times 1{\cdot}65 \times 10^{-24}$, we obtain $\lambda_{-1} \simeq 6{\cdot}7 \times 10^{-10}\nu$. For a pressure of 200 mm. Hg at 800° K. we have $\nu = 2{\cdot}4 \times 10^{18}$ so that at this pressure $\lambda_{-1} \simeq 1{\cdot}6 \times 10^9 \text{ sec.}^{-1}$, about double $\lambda_0$. With the values of $\epsilon^*$, $\lambda_0$, $s$ chosen we should thus expect the rate to fall off at pressures of the order 200 mm. Hg in agreement with the facts.

(2) *Decomposition of gaseous dimethyl ether.* This is very similar. The final result of the reaction is

$$CH_3.O.CH_3 \rightarrow CH_4 + H_2 + CO,$$

proceeding at a convenient rate in the range 700–825° K.; it is first order down to a pressure of 400 mm. Hg. A pressure of 400 mm. Hg of admixed $H_2$ at 775° K. will preserve the first order rate to a pressure of 30 mm. Hg of the reactant. $N_2$, He, CO and $CO_2$ have no such effect. The first order rate constant can be represented empirically by the approximate equation

$$k_1 = 1{\cdot}5 \times 10^{13} e^{-29,450/T} \text{ sec.}^{-1},$$

or equally well by

$$k_1 = 1{\cdot}7 \times 10^9 . \frac{1}{5!}\left(\frac{33,250}{T}\right)^5 e^{-33,250/T} \text{ sec.}^{-1},$$

corresponding to a choice $s = 6$ and $\lambda_0 = 1{\cdot}7 \times 10^9 \text{ sec.}^{-1}$. For the number of deactivating collisions per unit time at 800° K. and 400 mm. Hg using (1215, 1) and setting $D = 10^{-7}$, $T = 800$, $m = 46 \times 1{\cdot}65 \times 10^{-24}$, $\nu = 4{\cdot}8 \times 10^{18}$, we obtain $\lambda_{-1} \simeq 4{\cdot}0 \times 10^9 \text{ sec.}^{-1}$ so that at this pressure $\lambda_0/\lambda_{-1} \simeq 0{\cdot}4$. With the chosen values of $\lambda_0$, $s$ the theory thus predicts a falling off of the rate at pressures somewhat below 400 mm. Hg in agreement with the facts.

Both these examples are entirely satisfactory, as are nearly a dozen others given in Table 1. We shall now give an example where the theory is less satisfactory.

(3) *Decomposition of nitrogen pentoxide.* This, the best known and most exhaustively investigated homogeneous unimolecular reaction, shows no signs of deviation from the unimolecular law down to pressures of 0·06 mm. Hg, but at about this pressure it has been shown that a distinct falling off in

* In the following calculations the values of $D$ are in cm., of $T$ in °K., of $m$ in g., of $\nu$ in molecules $\text{cm.}^{-3}$ and of $\lambda_0$, $\lambda_{-1}$ in $\text{sec.}^{-1}$.

the rate sets in. The convenient temperature range is from 273° K. to 340° K. *No effect of any diluent in maintaining the rate at pressures below 0·06 mm. Hg has been recorded. Admixtures of numerous gases have been shown to be without effect on the rate of the reaction.* The result of the reaction is

$$N_2O_5 \rightarrow N_2O_4 + \tfrac{1}{2}O_2,$$

but of course this does not represent the actual mechanism. The first order rate constant can be expressed empirically by the equation

$$k_1 = 4{\cdot}1 \times 10^{13} e^{-12{,}380/T} \text{ sec.}^{-1}$$

or with equal accuracy by

$$k_1 = 1{\cdot}8 \times 10^6 . \frac{1}{14!} \left(\frac{16{,}550}{T}\right)^{14} e^{-16{,}550/T} \text{ sec.}^{-1}$$

corresponding to a choice of $s = 15$ and $\lambda_0 = 1{\cdot}8 \times 10^6$ sec.$^{-1}$. We have to compare this with the rate of deactivation at 300° K. and 0·06 mm. Hg. Using formula (1215, 1) and setting $D = 10^{-7}$, $T = 300$, $m = 108 \times 1{\cdot}65 \times 10^{-24}$, $\nu = 1{\cdot}3 \times 10^{15}$, we obtain $\lambda_{-1} \simeq 1{\cdot}4 \times 10^6$ sec.$^{-1}$. Thus the values chosen for $\lambda_0$ and $s$ correspond to a falling off from the first order rate at pressures of the order 0·06 mm. Hg in agreement with experiment. No smaller value of $s$ will suffice to give this agreement, and it is rather disturbing that such a large value for $s$ is required. Apparently the only way of avoiding such a large value for $s$ is the use of a larger value for $D$, the effective diameter for deactivating collisions, or an equivalent assumption.

§ **1217. Improved theory.** Hitherto we have assumed the same probability $\lambda_0$ of decomposition in unit time for all active molecules whatever the energy in the $s$ internal vibrations provided it exceeds $\epsilon^*$. Alternatively $\lambda_0$ may be thought of as an average value for all types of active molecules. This approximation is sufficient to predict approximately at what pressure the rate will cease to be first order, but a more accurate approximation is required to account for the details of the rate in the pressure range where the rate is changing from first order to second order. Such a theory has been developed by Rice and Ramsperger,† and independently by Kassel.‡ It is reasonable to suppose that for decomposition to occur it is necessary for a certain minimum energy to become concentrated in one particular internal vibration, and it is almost certain that this has a better chance of occurring the greater the energy distributed amongst $s$ internal vibrations including this particular one. Certain plausible assumptions about the redistribution of energy among the $s$ degrees of freedom lead to a probability for decomposition in unit time for molecules of energy $\epsilon$ proportional to $(1 - \epsilon^*/\epsilon)^{s-1}$. Ramsperger tested this theory on all the then known unimolecular reactions.

† Rice and Ramsperger, *J. Am. Chem. Soc.* **49**, 1617 (1927).

‡ Kassel, *J. Phys. Chem.* **32**, 225 (1928).

TABLE 1

*Ramsperger's analysis of data for unimolecular reactions*

| Reactant | Temperatures °K. | Pressures cm. Hg | $P$ sec.$^{-1}$ | $Q/k$ deg. | Number $s$ of classical vibrations | References |
|---|---|---|---|---|---|---|
| $N_2O_5$ | 273–338 | 0·00019 to 70 | $4·5 \times 10^{13}$ | 12,350 | 15 | (1) |
| $C_2H_5CHO$ | 723–873 | 2·0 to 40 | $> 1·4 \times 10^{12}$ | 27,000 | 6 | (2) |
| $d$-$C_{10}H_{16}$ | 457 510 | 17 to 116 | $5·4 \times 10^{14}$ | 21,850 | > 10 | (3) |
| $CH_3N=NCH_3$ | 551–603 | 0·026 to 70 | $1·1 \times 10^{16}$ | 25,600 | 13 | (4) |
| $C_2H_5—O—C_2H_5$ | 699–861 | 2·5 to 50 | $> 3·1 \times 10^{11}$ | 26,500 | 3 | (5) |
| $CH_3—O—CH_3$ | 695–825 | 3·0 to 90 | $1·9 \times 10^{13}$ | 29,250 | 6 | (6) |
| $C_3H_7N=NC_3H_7$ | 523–563 | 0·025 to 4·6 | $5·6 \times 10^{13}$ | 20,450 | > 20 | (7) |
| $H_2C—CH_2$ (with O bridging) | 651–718 | 2·4 to 90 | $8·4 \times 10^{12}$ | 26,000 | > 7 | (8) |
| $CH_3.N=NC_3H_7$ | 523–605 | 0·0058 to 13 | $2·8 \times 10^{15}$ | 23,740 | 17 | (9) |
| $CH_3—O—C_2H_5$ | 659–733 | 2·6 to 54 | $1·2 \times 10^{12}$ | 23,500 | 4 | (10) |
| $CH_3—O—C_3H_7$ | 673–723 | 2·2 to 33 | $4·5 \times 10^{12}$ | 24,500 | 6 | (10) |
| $N_2O$ | 833–940 | 8·1 to 800 | $4·0 \times 10^{9}$ | 26,500 | 1 | (11) |
| $C_2H_5NH_2$ | 773–813 | 5·0 to 40 | $2·9 \times 10^{9}$ | 21,700 | 3 | (12) |
| $CH_3N=N—NHCH_3$ | 473–503 | 0·019 to 8 | $4·1 \times 10^{11}$ | 16,900 | 7 | (13) |
| $Cl.CO.OCCl_3$ | 533–583 | 0·4 to 1·7 | $1·4 \times 10^{13}$ | 20,750 | > 14 | (14) |

*References to Table 1*


(1) Daniels and Johnston, *J. Am. Chem. Soc.* **43**, 53 (1921).
Ramsperger and Tolman, *Proc. Nat. Acad. Sci.* **16**, 6 (1930).
Schumacher and Sprenger, *Proc. Nat. Acad. Sci.* **16**, 129 (1930).
Hodges and Linhorst, *Proc. Nat. Acad. Sci.* **17**, 28 (1931).

(2) Hinshelwood and Thompson, *Proc. Roy. Soc.* A, **113**, 221 (1926).

(3) Smith, D. F., *J. Am. Chem. Soc.* **49**, 43 (1927).
Kassel, *J. Am. Chem. Soc.* **52**, 1935 (1930).

(4) Ramsperger, *J. Am. Chem. Soc.* **49**, 912 (1927).
Ramsperger, *J. Am. Chem. Soc.* **49**, 1495 (1927).

(5) Hinshelwood, *Proc. Roy. Soc.* A, **114**, 84 (1927).

(6) Hinshelwood and Askey, *Proc. Roy. Soc.* A, **115**, 215 (1927).

(7) Ramsperger, *J. Am. Chem. Soc.* **50**, 714 (1928).

(8) Heckert and Mack, *J. Am. Chem. Soc.* **51**, 2706 (1929)

(9) Ramsperger, *J. Am. Chem. Soc.* **51**, 2134 (1929).

(10) Glass and Hinshelwood, *J. Chem. Soc.* p. 1804 (1929).

(11) Volmer and Kummerow, *Zeit. Physikal. Chem.* B, **9**, 141 (1930).
Nagasako and Volmer, *Zeit. Physikal. Chem.* B, **10**, 414 (1930).
Ramsperger and Waddington, *Proc. Nat. Acad. Sci.* **17**, 103 (1931).

(12) Taylor, H. A., *J. Phys. Chem.* **34**, 2761 (1930).

(13) Ramsperger and Leermakers, *J. Am. Chem. Soc.* **53**, 2061 (1931).

(14) Ramsperger and Waddington, Unpublished data quoted by Ramsperger, *Chem. Rev.* **10**, 27 (1932).

We cannot give details,* but will merely mention that for all such reactions, as have been studied in the pressure range where the rate is changing from first order to second order, Ramsperger is able to account for the rates observed by assuming not unreasonable values for $s$, the number of classical vibrations that contribute to the energy of activation. Table 1 summarizes the most reliable data for unimolecular reactions. The first column gives the substance which decomposes by a unimolecular mechanism. The second and third give the temperature and pressure ranges over which the rate has been studied. The fourth and fifth columns give the parameters $P$, $Q$ in the empirical formula for the first order rate constant

$$k_1 = Pe^{-Q/kT}. \qquad (1217, 1)$$

The sixth column gives the approximate values of $s$ estimated by the theory outlined above. There is no apparent connection between these values and the structure of the decomposing molecule.

Since the compilation of Table 1, it has been shown by Hinshelwood† and others that some of the tabulated reactions can take place by two alternative mechanisms, (1) direct rearrangement to stable products, and (2) the production of free radicals which may cause further decomposition by a chain process. The relative importance of the two mechanisms has been studied by the addition of traces of nitric oxide, which destroys the free radicals and so breaks the chains. The recognition of the part played by radicals does not necessitate any fundamental change of view about the nature of unimolecular reactions. It is, however, necessary to repeat the whole numerical analysis for the chain free process when the effects of the chains have been eliminated. Staveley and Hinshelwood have done this and find for the unimolecular decompositions of various ethers the values given in Table 2. These revised values of $s$ certainly vary with the com-

TABLE 2

*Revised data for unimolecular decompositions of ethers*

| Reactant | $Q/k$ for chain-free reaction deg. | Number $s$ of classical vibrations |
|---|---|---|
| $CH_3—O—CH_3$ | 31,000 | 5 |
| $CH_3—O—C_2H_5$ | 31,000 | 5 |
| $C_2H_5—O—C_2H_5$ | 33,500 | 9 |
| $C_3H_7—O—C_3H_7\,(n)$ | 30,250 | 9 |
| $C_3H_7—O—C_3H_7\,(i)$ | 32,750 | $>12$ |

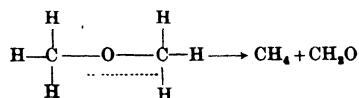
* For details and complete references see Ramsperger, *Chem. Rev.* **10**, 27 (1932), or Kassel, *Kinetics of Homogeneous Gas Reactions*, Chapters v, x.

† Staveley and Hinshelwood, *J. Chem. Soc.* p. 1568 (1937).

plexity of the ether in a more reasonable way than the earlier computed values. In particular the revised value of $s$ for $CH_3$—O—$CH_3$ is less than that for $C_2H_5$—O—$C_2H_5$. Other unimolecular reactions may require similar revision.

**§ 1218. Absolute values of unimolecular rates.** The probability of decomposition in unit time of an active molecule, which we have denoted by $\lambda_0$, has the dimensions of a frequency. It is clear that $\lambda_0$ is not the frequency of any normal mode, but is rather a frequency of interchange of energy between normal modes. The calculation *a priori* of $\lambda_0$ therefore requires a detailed consideration of interaction between the various normal modes. This is a problem in quantum theory and evidently a complicated one. A satisfactory solution of it can hardly be expected at present.

What can be said with confidence at the present time is more or less as follows. For a molecule to dissociate it is necessary that sufficient energy shall accumulate into one particular bond or perhaps two bonds in the molecule, the bonds in question being those which are broken in the normal process of decomposition. If for example the primary process in the decomposition of dimethyl ether is

```
   H          H
   |          |
H—C————O————C—H ——→ CH₄+CH₂O
   |    ......|
   H          H
```

then it is one C—O bond and one C—H bond that have to be stretched sufficiently for the H atom to "collide" with and become attached to the $CH_3$ radical. It is alternatively possible, though less probable, that the primary process is the simple splitting of the bond between the $CH_3$ and the O—$CH_3$ radicals. The energy required for the latter mechanism will probably be greater than that required for the former one and consequently the former mechanism seems the more likely. Nevertheless, for the sake of simplicity, we shall discuss the case where only one bond is involved.

The internal motion of a complicated molecule can be resolved into a number of normal modes, which are approximately harmonic oscillations of (in general) incommensurable frequencies. All the usual coordinates which might be used to define the configuration of the molecule can be expressed in terms of the normal coordinates which correspond to the normal modes, and the variation of any such coordinate can be expressed in terms of a number of harmonic terms one from each normal mode. In general, contributions from every normal mode will enter into the variation of any one ordinary geometrical coordinate, and so the energy in every normal mode can contribute to the energy necessary to overcome the potential hill. The

problem of calculating how soon on the average a molecule with more than enough energy will dissociate is the problem, therefore, of calculating how soon on the average the vital coordinate will exceed a given value, when it is the resultant of a number of approximately harmonic terms with incommensurable frequencies, whose amplitudes are controlled by the total energy allowed to the molecule and whose relative phases have all possible values. This is a classical description, but the quantal description may be made to correspond closely. The details of such a calculation are far from clear, even for the simple classical model, but some progress based on general principles has been made recently by Slater,† who has used this model to calculate upper and lower bounds for the dissociation rate per molecule with sufficient total energy. The formulae obtained for these bounds are not simple, but one strikingly simple approximate result emerges. If we denote by $\epsilon^*$ the minimum total vibrational energy the molecule must have to be able to dissociate, then the first order rate constant $k_1$ will be roughly given by

$$k_1 \simeq \bar{\lambda} e^{-\epsilon^*/kT}, \qquad (1218, 1)$$

where $\bar{\lambda}$ has the dimensions of a frequency and is of the order of magnitude of the frequencies of the normal modes. This $\bar{\lambda}$ is not independent of temperature, and so $\epsilon^*$ is not equal to the energy of activation; however $\epsilon^*$ will probably not differ greatly from the energy of activation. It is therefore interesting to note that when the rates of various unimolecular reactions are expressed in the empirical form (1217, 1) the majority of values of $P$ in fact lie in the range $10^{13}$ to $10^{14}$ sec.$^{-1}$ (see examples in § 1216), which coincides closely with the range of frequencies of the normal modes. More accurate absolute theoretical estimates of unimolecular rates are at present beyond practical reach.

**§ 1219. Reactions in solution.** Reactions in solution naturally present a far more formidable problem than reactions in a gas, which may normally be assumed to be almost perfect. None the less the recent developments in the theory of liquids, outlined in Chapter VIII, have been sufficiently successful to enable tentative advances to be made in the theory of reactions in dilute solutions, based on a model and approximations which, though crude, are not so crude as to be unreliable.

We base the discussion therefore on the model of a liquid in which we assume that each molecule is in thermal agitation in a cage or cell formed by its nearest neighbours in a more or less (locally) regular way. In the simplest liquids the average number of neighbours may be expected to be twelve. For the sake of simplicity we shall use the smoothed potential model of § 802. We accordingly assume that, for the purposes of this discussion, the

† N. B. Slater, *Proc. Camb. Phil. Soc.* **35**, 56 (1939).

cell in which the centre of any molecule may move is a region of constant potential energy, and that the molecules themselves are rigid spheres of diameter $D_0$. This diameter will be assumed to be approximately that attributed to similar molecules in the gas phase. If the liquid molecules are arranged more or less in a close packed (irregular) way, and the mean separation of nearest neighbours is $D$, then it may be shown that the relationship between $D$ and $\nu$ the total number of molecules per unit volume is

$$\nu D^3 = \sqrt{2}. \tag{1219, 1}$$

The separation $D$ will be greater than $D_0$ and will depend on the temperature. A rough approximation will be to write

$$D = D_0 + a, \tag{1219, 2}$$

and take $a$ for the radius of the cell to which any particular molecule is in general confined. It will be clear from Chapter VIII that, though we are thus using a very crude simplification of the successful model there introduced, we have retained its essential features, and may expect to find that it is a rough but reliable tool for a preliminary study of collision numbers and reaction rates in solutions. In using it in this way, however, we must recognize that we must assume that the solute molecules fit without much distortion into the same general pattern as those of the pure solvent, and that it will be necessary to treat the motion of every molecule in its cell as classical. The cells concerned are small, and it may be shown that classical methods are barely good enough and may introduce some errors, though probably not serious ones.* We thus assign to the molecules in their cells a classical distribution both in position and in velocity. Then the average fraction of a molecule per unit volume of each cell of radius $a$, moving with velocity in the range $V, V+dV$ in a direction lying within the solid angle $d\omega$, is by (303, 7)

$$\left(\frac{m}{2\pi kT}\right)^{\frac{3}{2}} e^{-\frac{1}{2}mV^2/kT}\, V^2 dV\, d\omega/\tfrac{4}{3}\pi a^3. \tag{1219, 3}$$

Now consider a molecule moving towards the wall at an angle with the normal between $\theta$ and $\theta+d\theta$. Such a molecule will hit the wall within a time $dt$ provided that at the beginning of this interval it lies within a distance $V\cos\theta\, dt$ of the wall, that is within a shell of volume $4\pi a^2 \cos\theta V dt$. The corresponding value of $d\omega$ is $2\pi \sin\theta\, d\theta$. Hence the average number of collisions of a given molecule with the cell wall per unit time, at velocity between $V$ and $V+dV$, making an angle with the normal between $\theta$ and $\theta+d\theta$, is

$$\left(\frac{m}{2\pi kT}\right)^{\frac{3}{2}} e^{-\frac{1}{2}mV^2/kT}\, V^2 dV\, 2\pi \sin\theta\, d\theta\, 4\pi a^2 V \cos\theta/\tfrac{4}{3}\pi a^3$$

$$= \frac{3}{a}\left(\frac{m}{2\pi kT}\right)^{\frac{3}{2}} e^{-\frac{1}{2}mV^2/kT}\, V^3 dV\, 2\pi \sin\theta \cos\theta\, d\theta. \tag{1219, 4}$$

* Fowler and Slater, *Trans. Fara. Soc.* **34**, 81 (1938).

Alternatively we may say that the number of collisions of a given molecule with the cell wall per unit time with total kinetic energy between $\epsilon$ and $\epsilon + d\epsilon$ and with angle of incidence between $\theta$ and $\theta + d\theta$ is

$$\frac{3}{a}\left(\frac{2kT}{\pi m}\right)^{\frac{1}{2}} e^{-\epsilon/kT} \frac{\epsilon}{kT}\frac{d\epsilon}{kT} \sin\theta \cos\theta \, d\theta. \qquad (1219, 5)$$

The total number of collisions per unit time of a given molecule with the cell wall is therefore given by

$$\frac{3}{a}\left(\frac{2kT}{\pi m}\right)^{\frac{1}{2}} \int_0^\infty e^{-\epsilon/kT} \frac{\epsilon}{kT}\frac{d\epsilon}{kT} \int_0^{\pi/2} \sin\theta \cos\theta \, d\theta. \qquad (1219, 6)$$

Performing the integrations, we thus obtain for the total number of collisions per unit time of a given molecule with the cell wall

$$\frac{3}{2a}\left(\frac{2kT}{\pi m}\right)^{\frac{1}{2}}. \qquad (1219, 7)$$

In an ideal mixture containing per unit volume altogether $\nu$ molecules, of which $\nu_1$ are of type 1, $\nu_2$ of type 2 and so on, we may expect that of all the collisions of a given molecule the fraction that strikes some molecule of a given type say 2 will be $\nu_2/\nu$. We deduce from (7) that the number $Z_{1\to 2}$ of collisions per unit volume and per unit time in which a molecule of type 1 hits a molecule of type 2 will be given by

$$Z_{1\to 2} = \frac{\nu_1 \nu_2}{\nu} \frac{3}{2a}\left(\frac{2kT}{\pi m_1}\right)^{\frac{1}{2}}. \qquad (1219, 8)$$

In making this calculation we have assumed that the molecules of type 1 are moving in their cages and hit molecules of type 2 forming part of the stationary walls. If on the other hand we had considered the molecules of type 2 as moving in their cages and the molecules of type 1 as forming part of the walls, we should have obtained instead of (8)

$$Z_{2\to 1} = \frac{\nu_1 \nu_2}{\nu} \frac{3}{2a}\left(\frac{2kT}{\pi m_2}\right)^{\frac{1}{2}}. \qquad (1219, 9)$$

Actually, of course, both suppositions are wrong, since the two types of molecule should be treated similarly, and the true formula should be symmetrical with respect to the species 1 and 2. One could obtain such a symmetrical formula by taking the sum of (8) and (9). We should thus obtain for the total number $Z_{12}$ of collisions per unit volume and per unit time between a molecule of type 1 and a molecule of type 2

$$Z_{12} = \frac{\nu_1 \nu_2}{\sigma_{12} \nu} \frac{3}{2a}\left(\frac{2kT}{\pi}\right)^{\frac{1}{2}} (m_1^{-\frac{1}{2}} + m_2^{-\frac{1}{2}}), \qquad (1219, 10)$$

where the symmetry number $\sigma_{12}$ is introduced as usual to prevent counting each collision twice over when the two molecules considered are of the same

species. An alternative formula, also symmetrical with respect to the species 1 and 2, is

$$Z_{12} = \frac{\nu_1 \nu_2}{\sigma_{12} \nu} \frac{3}{2a} \left(\frac{2kT}{\pi}\right)^{\frac{1}{2}} \left(\frac{1}{m_1} + \frac{1}{m_2}\right)^{\frac{1}{2}}$$

$$= \frac{\nu_1 \nu_2}{\sigma_{12} \nu} \frac{3}{2a} \left(\frac{2kT}{\pi\mu}\right)^{\frac{1}{2}}, \qquad (1219, 11)$$

where $\mu = m_1 m_2/(m_1 + m_2)$ is the reduced mass. Neither (10) nor (11) has any exact sound basis, but either may be accepted as a reasonable approximation. We can safely use either (10) or (11) as giving the correct order of magnitude of the collision number $Z_{12}$. As a matter of convenience we shall use (11). Using the relation (1) for a close packed liquid, we can rewrite (11) as

$$Z_{12} = \frac{\nu_1 \nu_2}{\sigma_{12}} \frac{3D^3}{2^{\frac{3}{2}} a} \left(\frac{2kT}{\pi\mu}\right)^{\frac{1}{2}}$$

$$= 2 \frac{\nu_1 \nu_2}{\sigma_{12}} \frac{3D^3}{2^{\frac{5}{2}} \pi a} \left(\frac{2\pi kT}{\mu}\right)^{\frac{1}{2}}. \qquad (1219, 12)$$

Comparing (12) with the corresponding formula (1201, 18) for collisions in the gas phase, we see that the gas formula may be applied to the liquid phase, provided we use an effective collision diameter $D_{\text{eff}}$ defined by

$$D_{\text{eff}}^2 = \frac{3}{2^{\frac{5}{2}} \pi} \frac{D^3}{a}, \qquad (1219, 13)$$

so that $D_{\text{eff}}$ is of the same order of magnitude as $D$. In fact $D_{\text{eff}}$ would be equal to $D$ if $(D - D_0)/D = a/D = 3/2^{\frac{5}{2}}\pi \simeq \frac{1}{6}$. Actually $a/D$ is probably somewhat less than this, and so $D_{\text{eff}}$ is probably somewhat greater than $D$. In any case we may safely assume that the ratio of the collision number in the liquid to that in the gas is not seriously different from unity.

A more important quantity for reaction rate theory is presumably the number of collisions with the cell wall per unit time in which the kinetic energy in the normal motion exceeds a given value $\epsilon^*$. Such collisions are specified by

$$1 \geqslant \cos\theta \geqslant (\epsilon^*/\epsilon)^{\frac{1}{2}} \quad (\epsilon > \epsilon^*). \qquad (1219, 14)$$

For each molecule this number is then given according to (5) by

$$\frac{3}{a}\left(\frac{2kT}{\pi m}\right)^{\frac{1}{2}} \int_{\epsilon^*}^{\infty} e^{-\epsilon/kT} \frac{\epsilon}{kT} \frac{d\epsilon}{kT} \int_{\cos\theta = 1}^{\cos\theta = (\epsilon^*/\epsilon)^{\frac{1}{2}}} \sin\theta \cos\theta \, d\theta. \qquad (1219, 15)$$

The integrations are straightforward and lead to

$$\frac{3}{2a}\left(\frac{2kT}{\pi m}\right)^{\frac{1}{2}} e^{-\epsilon^*/kT}. \qquad (1219, 16)$$

If we denote by $Z_{12}$ the total number per unit volume and per unit time of collisions between two molecules of types 1 and 2, and the number of

these with energy in the normal direction† exceeding $\epsilon^*$ by $Z_{12}(\epsilon^*)$, comparison of (16) with (7) shows that

$$Z_{12}(\epsilon^*) = Z_{12}e^{-\epsilon^*/kT}. \tag{1219, 17}$$

This has the same form as (1201, 22) for collisions in the gas.

We do not propose here to give further details,‡ but shall content ourselves with a qualitative discussion. It is desirable, however, to start as we have done by making quite clear the exact type of model of a liquid, on which even a qualitative discussion is based.

In this model any molecule and its neighbours must not be thought of as permanently fixed in the relationship of "neighbourliness". The central molecule will occasionally escape from its cell by exchanging with a molecule on the cell wall, and the molecules on the cell wall will not be permanent but will occasionally be replaced by others by the process of diffusion or self-diffusion. If we denote by a collision between two molecules, particularly two solute molecules, any event in which one of them approaches and rebounds from the other, which is then necessarily a member of its cell wall, it may be verified by calculation—and is indeed almost obvious—that in general one pair of such molecules will make many collisions while they remain neighbours before they are divorced by the natural processes of diffusion. This is a feature of collisions in dilute solution which is foreign to collisions in gases. In general, in gases a collision between a given pair of molecules is hardly ever immediately repeated and such repetitions as do occur are always and rightly neglected. In studying collisions in dilute solutions it may therefore sometimes be necessary to distinguish between fresh collisions and repetitive collisions between a single pair. We shall call the whole group of collisions, which occur between a single pair of molecules after they become neighbours and before they separate again, an *encounter*.

We have seen that it is possible to obtain rough but reliable estimates for the total number of collisions per unit volume and per unit time between two molecules of given types, and also for the number of such collisions in which the kinetic energy along the line of centres exceeds a given value $\epsilon^*$. We found that these numbers differ only slightly from those in a gas for the same concentrations. We conclude that the rate of bimolecular reaction in dilute solutions may be expected *in general* to be about the same as that for the same molecules at the same concentration in a gas. Various provisos must, however, be satisfied for this conclusion to hold. In the first place the

† According to the derivation given, this means normal to the cell wall of one of the molecules and it is not clear which. What is really wanted is the direction along the line of centres at impact. The inaccuracy here introduced is probably not serious.

‡ For a more detailed discussion see: Fowler and Slater, *Trans. Fara. Soc.* **34**, 81 (1938). Compare Rabinowitch, *Trans. Fara. Soc.* **33**, 1225 (1937), where a very similar discussion is presented.

arguments we have adduced do not apply to solute molecules of very different size and shape from the molecules of the solvent. The conclusion may well remain true in such a case, but we have given no theoretical grounds for expecting that it will. In the second place the conclusion may be upset if the reacting solute molecules are intimately associated in any way (solvated) with the molecules of the solvent. Thirdly the reaction rate must not be so fast that, according to the equilibrium formula for collision numbers, more than one reactive collision should occur during a single encounter except very rarely. Once a reaction has occurred between a pair of molecules further collisions, which would otherwise have occurred between them during the same encounter, are necessarily futile, but they are counted in the estimate of the energetic collision rate, which is made up in solution of bunches of collisions provided by each encounter, instead of by the quite separate single collisions of the gas phase. In the extreme limit of reactions for which the rate is fast compared with the rate of the starting of encounters, one will reach a state of affairs in which every encounter leads to a reaction, and the reaction rate is then controlled by the encounter rate and the coefficient of diffusion, instead of by the energetic collision rate as in a gas. Rates of reaction usually studied are not so fast as this, and conform rather to the other limit in which the likelihood of reaction during each encounter is low. The reaction rate is then, the other provisos being also satisfied, correctly given by the energetic collision rate, which is substantially the same as for a gas at the same concentrations of the reactants.

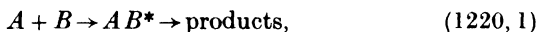
The same general conclusions can be drawn by following out the method of the activated complex applied to dilute solutions. Provided that neither the activated complex nor the separated solute molecules are intimately associated in any special way with the solvent molecules, we can assign partition functions to these molecules and the complex in the solution, using for each a suitable cell in the liquid; it is not now essential to the argument to assume that these cells are so closely similar to the cells of the solvent molecules themselves. The partition functions so assigned will differ from the partition functions for the same molecules or complex in the gas phase only by having a suitable free volume factor in place of the actual volume. To the accuracy of this formulation the concentration of activated complexes in the solution, and the rate at which they enter into reaction, and therefore the rate of the reaction itself, will be substantially the same as for the gas phase at the same concentrations of the reactants. To this approximation the method of the activated complex is substantially equivalent to the collision method and leads to the same conclusions.* The method of the activated complex, however, presents opportunities of formally taking

* Cf. Bell, *Trans. Fara. Soc.* **35**, 324 (1939).

account of the way in which the reaction rate may be affected by the presence of the solvent molecules in a manner which seems out of the question in the method of collisions. It is hardly fair to claim that much progress has yet been made in this direction, owing to our almost complete ignorance of the details of interaction between solute and solvent molecules.

Although the application of the method of the activated complex to the calculation of absolute rates can as yet take us no further than the cruder collision theory, it can be useful in calculating the effect on the rate of small changes of environment. In particular the primary kinetic salt effects, discussed in detail in the following section, may be regarded as a particularly fruitful special case. Actually this special application preceded the general formulation of the method by about twelve years.

**§ 1220. Primary kinetic salt effects.** Although it is not generally possible to predict the effect on a reaction rate of changing the solvent, there is one case where this can be done fairly accurately. For any reaction involving ions one can predict the effect on the reaction rate of adding an inert electrolyte; the word inert signifies that the added electrolyte does not itself take part in the reaction. It will suffice to confine ourselves to bimolecular processes. Let the process be

$$A + B \rightarrow AB^* \rightarrow \text{products}, \qquad (1220, 1)$$

where at least one of the molecules $A$ and $B$ is an ion and $AB^*$ denotes the activated complex. Then, subject to certain restrictions discussed in § 1211 and to which we shall not refer again, the rate is proportional to the concentration of the complex $AB^*$, which in the absence of chemical reaction would be in equilibrium with the free molecules (or ions) $A$ and $B$. This equilibrium will be affected by all the ions present according to the considerations of Chapter IX. By introducing the activity coefficients defined in § 903 we can express this equilibrium in the form

$$\frac{\nu_{AB^*}}{\nu_A \nu_B} = K^0 \frac{\gamma_A \gamma_B}{\gamma_{AB^*}}, \qquad (1220, 2)$$

where $\nu$ denotes a concentration of ions or molecules per unit volume, and $\gamma$ denotes an activity coefficient, while $K^0$ is an equilibrium constant depending on the solvent and the temperature but independent of the solute concentrations. But since the reaction rate is proportional to the equilibrium concentration $\nu_{AB^*}$, the second order rate constant must be proportional to $\nu_{AB^*}/\nu_A \nu_B$. Hence by (2) the rate constant $k$ will be given by

$$k = k^0 \gamma_A \gamma_B / \gamma_{AB^*}, \qquad (1220, 3)$$

where $k^0$ is determined by the temperature and solvent, but is independent

of the solute concentrations. Formula (3) is due to Brönsted† but the above derivation is essentially that of Bjerrum.‡

The utility of formula (3) is completely dependent on the possibility of evaluating $\gamma_{AB^*}$, the activity coefficient of the activated complex. If we confine ourselves to solutions so dilute that they would be ideal were it not for the interionic electrostatic forces, then we can apply the formulae of Chapter IX to the evaluation of $\gamma_{AB^*}$ as well as $\gamma_A$ and $\gamma_B$. As we require the activity coefficients of several species in a mixed solution, it is most convenient to use the approximate theory of § 926. We assume the solvent to be water and the temperature to be between 15° C. and 25° C. If then we denote by $z_A$, $z_B$ the valencies of the two reacting molecules or ions, we have

$$\log_{10}\gamma_A = -0{\cdot}5\frac{z_A^2 I^{\frac{1}{2}}}{1+I^{\frac{1}{2}}} + l_A I, \tag{1220, 4}$$

where $I$ denotes the ionic strength and $l_A$ depends on the nature of the species $A$ as well as the nature of all the other ions present, but remains constant if the solution as a whole is concentrated or diluted keeping the relative solute concentrations unaltered. Similarly for the species $B$

$$\log_{10}\gamma_B = -0{\cdot}5\frac{z_B^2 I^{\frac{1}{2}}}{1+I^{\frac{1}{2}}} + l_B I, \tag{1220, 5}$$

where $l_B$ is another specific constant. As regards the activated complex $AB^*$, whatever its structure, its valency is equal to the algebraic sum $(z_A + z_B)$ of the valencies $A$ and $B$. Hence we have the formula

$$\log_{10}\gamma_{AB^*} = -0{\cdot}5\frac{(z_A+z_B)^2 I^{\frac{1}{2}}}{1+I^{\frac{1}{2}}} + l_{AB^*} I, \tag{1220, 6}$$

where $l_{AB^*}$ is another specific constant. Combining (4), (5) and (6), we derive

$$\log_{10}\frac{\gamma_{AB^*}}{\gamma_A\gamma_B} = 1{\cdot}0\frac{z_A z_B I^{\frac{1}{2}}}{1+I^{\frac{1}{2}}} + lI, \tag{1220, 7}$$

where $l$ is a specific constant determined by the relative concentrations of the various ionic species. Substituting from (7) into (3), we obtain

$$\log_{10} k = \log_{10} k^0 + 1{\cdot}0\frac{z_A z_B I^{\frac{1}{2}}}{1+I^{\frac{1}{2}}} + lI. \tag{1220, 8}$$

The dependence of $k$ on the ionic strength was named by Brönsted the *primary kinetic salt effect*, to distinguish it from the *secondary kinetic salt effect* which will be described in the next section.

The limiting form of (8) at very high dilutions is

$$\log_{10} k = \log_{10} k^0 + 1{\cdot}0 z_A z_B I^{\frac{1}{2}}. \tag{1220, 9}$$

† Brönsted, *Zeit. Physikal. Chem.* **102**, 169 (1922).
‡ Bjerrum, *Zeit. Physikal. Chem.* **108**, 82 (1923).

From this we see that in very dilute solutions the rate constant should increase (*positive kinetic salt effect*) with increase of ionic strength for all reactions between two ions of the same sign and should decrease (*negative kinetic salt effect*) with increase of ionic strength for all reactions between ions of opposite sign. A plot of $\log k$ against the ionic strength gives a parabola in both cases and such kinetic salt effects may therefore be referred to as parabolic. For processes involving only one ion ($z_A$ or $z_B$ zero) formula (9) predicts zero kinetic salt effect. Actually the effect will not be zero, but will be determined by the term $lI$ in (8). For such reactions then $\log_{10} k$ is linear in the ionic strength and such an effect is called a linear kinetic salt effect.

It is difficult to make accurate measurements at sufficiently high dilutions for (9) to be valid, but all the reliable data in dilute solutions show kinetic salt effects of the sign predicted by the theory, and a plot of $\log k$ against $I^{\frac{1}{2}}$ gives a curve with a slope at $I = 0$ equal, within the experimental error, to the predicted value $1{\cdot}0 z_A z_B$. This is shown in Fig. 3 for a number of reactions of various valency types.*

It is perhaps of interest to derive formula (9) by more directly statistical reasoning. Let us suppose that the reaction rate is proportional to the number of pairs of molecules $A$ and $B$ in unit volume which approach each other within a distance $r$ in unit time. With the usual qualifications for the applicability of equilibrium theory, this is proportional to the number of pairs of molecules $A$ and $B$ at a distance between $r$ and $r + \Delta r$ in equilibrium with all the molecules $A$ and $B$. Now according to Debye's formula (911, 8) the mean electrostatic potential at a distance $r$ from the centre of a given ion $A$ is

$$\psi(r) = \frac{z_A |e|}{Dr} \frac{e^{-\kappa(r-a)}}{1+\kappa a}, \tag{1220, 10}$$

where $\kappa$ is defined by (911, 3), and $a$ is the average closest distance of approach of the two ions. But if $\nu_B$ denotes the number per unit volume of ions of type $B$ in the bulk of the solution, the number per unit volume at a distance $r$ from a given ion $A$ will according to Boltzmann's formula (subject to the approximation of § 910) be equal to $\nu_B e^{-z_B|e|\psi(r)/kT}$. The rate of reaction will therefore be proportional to $\nu_A \nu_B e^{-z_B|e|\psi(r)/kT}$, and so the second order rate constant will be proportional to $e^{-z_B|e|\psi(r)/kT}$. We may therefore write

$$\begin{aligned} \log k &= -z_B|e|\,\psi(r)/kT + \text{const.} \\ &= -\frac{z_A z_B |e|^2}{DrkT} \frac{e^{-\kappa(r-a)}}{1+\kappa a} + \text{const.} \end{aligned} \tag{1220, 11}$$

* This figure is taken from a paper by Livingston, *J. Chem. Educ.* 7 (12), 2899 (1930). In the original paper the reaction showing no appreciable salt effect was labelled wrongly. The error has persisted in several other copies of this figure (private communication from the author).

The additive constant is determined by the value of $k$ at infinite dilution ($\kappa = 0$); denoting this value by $k^0$, we obtain

$$\log k = \log k^0 - \frac{z_A z_B |e|^2}{DrkT}\left\{\frac{e^{-\kappa(r-a)}}{1+\kappa a} - 1\right\}. \qquad (1220, 12)$$

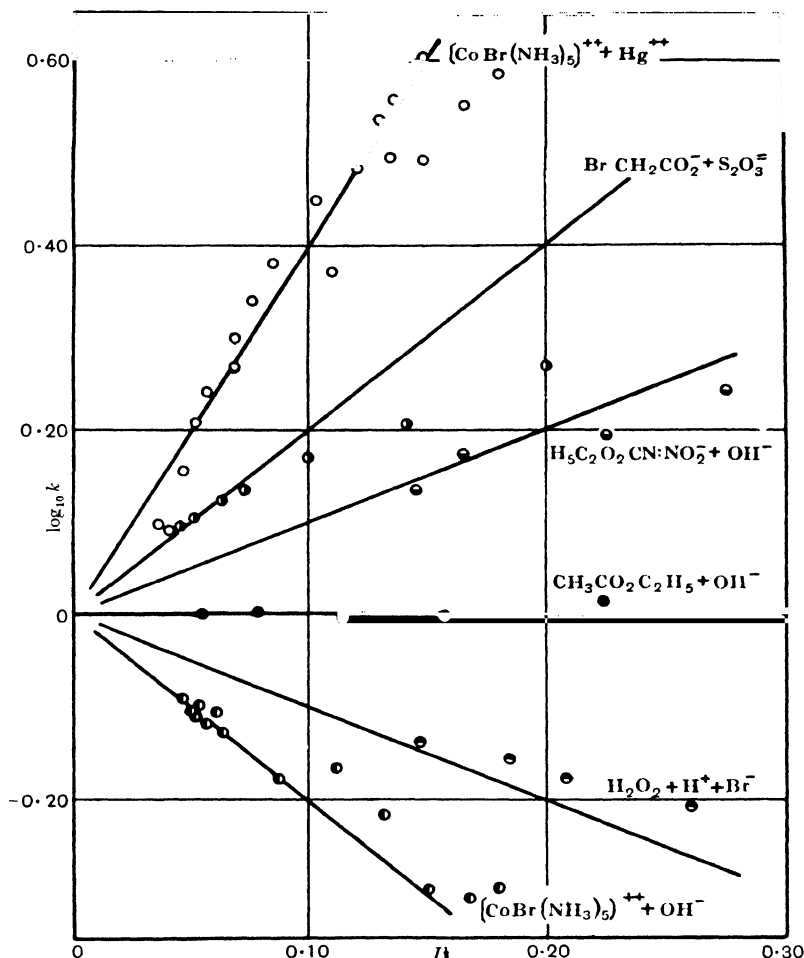



Fig. 3. The effect of ionic strength on the velocity of ionic reactions.

If we expand in powers of $\kappa$, we obtain

$$\log k = \log k^0 + \frac{z_A z_B |e|^2}{DkT}\kappa\left\{1 - \frac{r^2+a^2}{2r}\kappa + O(\kappa^2)\right\}. \qquad (1220, 13)$$

If we neglect all terms of higher order than the first in $\kappa$, we obtain

$$\log k_2 = \log_{10} k^0 + \frac{z_A z_B |e|^2}{DkT} \kappa. \qquad (1220, 14)$$

When numerical values are inserted for water at 20° C., this becomes formula (9). This derivation is due to Scatchard.*

**§ 1221. Secondary kinetic salt effects.** Sometimes the concentration of one of the reacting species is itself determined by an equilibrium which is affected by the ionic concentration. The best known examples are processes in which one of the reacting species is a hydrogen ion, the controlling equilibrium being of the type

$$\text{Acid} \rightleftarrows H^+ + \text{Base}, \qquad (1221, 1)$$

for example

$$H_2PO_4^- \rightleftarrows HPO_4^{--} + H^+. \qquad (1221, 2)$$

Addition of an inert electrolyte will shift the acid-base equilibrium and so indirectly affect the rate. This phenomenon was explained by Brönsted,† who called it a secondary kinetic salt effect to distinguish it from the primary effect discussed above. Since the effect is an equilibrium phenomenon, it obeys the laws of mass action modified by the interionic effects of Chapter IX, and there is no need to discuss it further.§

* Scatchard, *Chem. Rev.* **10**, 233 (1932). Compare Christiansen, *Zeit Physikal Chem* **113**, 35 (1924).

† Brönsted, *J. Chem. Soc.* **119**, 579 (1921).

§ See for example Bronsted and Teeter, *J. Phys. Chem.* **28**, 579 (1924); Brönsted and King, *J. Am. Chem. Soc.* **47**, 2523 (1925).

## CHAPTER XIII

### LATTICE IMPERFECTIONS, ORDER-DISORDER IN CRYSTALS

**§ 1300. Introduction.** In Chapter IV we have constructed partition functions and therewith thermodynamic potentials for crystalline solids, both pure and simple mixed. In all that discussion, however, we have assumed that the arrangement of the atoms or molecules on the proper lattice points is perfect, as in fact, as a rule, it very nearly is at all possible temperatures. In the case of mixed crystals so far studied we have assumed that the two or more sorts of molecule present are arranged at random on the available lattice points, but still that the molecules occupy all the lattice points available and are found in no other positions. These assumptions, (*a*) of the absence of lattice imperfections in pure or mixed crystals, and (*b*) of the absence of order among the constituents of a mixed crystal, are the natural starting-point for any theoretical study of crystals, but they form a first approximation only, and the basis of the study must now be widened.

It is, as we shall show, *a priori* necessary to expect that lattice imperfections will occur at all temperatures. The rearrangement of molecules required, for example, to leave one lattice point inside a crystal vacant, or to insert a molecule in a gap between others properly located on lattice points, requires only a finite amount of energy, so that such configurations must be found to some degree in the equilibrium state. It will be our first purpose to calculate the equilibrium concentration of such imperfections more closely defined. Besides the theoretical necessity for such imperfections there are numerous phenomena whose explanation may be said to require them. The diffusion of one type of atom into a lattice of another type to form a lattice of the mixture is a well-attested phenomenon. This requires the eventual substitution of one atom on a lattice point by an atom of the second type. Such a substitution could ideally occur by two atoms on neighbouring lattice points changing places. From the simplest geometrical and energetic considerations it is impossible to believe that such an elementary exchange can be anything but excessively rare, so rare that one cannot expect it to be of any importance in actual diffusion. There is energetically perhaps somewhat less objection to an elementary process in which 3, 4 or more atoms on a ring of lattice points simultaneously move so as to rotate the ring as a whole, but this is too far-fetched. The only reasonable explanation is that the primary process is the formation of lattice imperfections of some type, either holes or interlattice atoms, which are maintained naturally at equilibrium concentrations. They at once provide a mechanism by which

diffusion can occur, by the further processes of the movement of an interlattice atom or of the filling of a hole; such processes are geometrically simple and do not require an exorbitant amount of energy. Diffusion moreover is not the only phenomenon which requires natural lattice imperfections for its explanation. The electrolytic conduction of alkali halides and of silver halides must be explained in a similar way, and also many of their photoconductive properties.

We start this chapter therefore with a study of the equilibrium concentrations of lattice imperfections of certain simple types, first in crystals of a single component, and secondly in crystals of a typical salt. From this we proceed to imperfections which consist of the presence of extra atoms of one component. These ideas are readily extended to consider the presence of foreign atoms in a lattice present either on lattice points or in interlattice positions. From this one is led to the general study of the solubility of foreign atoms in crystalline solids, and we make a special study of the solubility of hydrogen in metals, particularly in palladium, a simple case, for which fairly complete calculations can be made and successfully compared with experiment.*

A rather different class of irregularity remains to be considered. This is the absence of complete order in a mixed crystal, such as a metallic alloy, in which the two components may be substituted for each other on any lattice point without too great a change in the configurational energy. The question here is no longer one of the absence of atoms from certain regular lattice points or their presence in interlattice positions, but of the regular or irregular arrangement of the two sorts of atoms on a given set of lattice points. The degree of order simply attainable is most marked when the two components are present in stoichiometric proportions, determined by the nature of the lattice. A state of perfect order is then possible in which a perfect atomic pattern is regularly repeated through the lattice, but such an ordered state can be realized (even in ideal conditions) only at the absolute zero. At higher temperatures there must always be some degree of disorder due to atomic interchanges, and it is the degree of this disorder as a function of the temperature which is the subject of study in the long closing sections of this chapter. It is a subject which has recently assumed considerable importance under the name of *order-disorder phenomena in metallic alloys*.

**§ 1301. Lattice imperfections in a simple pure crystal.** We shall start by considering the simplest possible case of lattice imperfections, that

* The theory of lattice imperfections has been largely developed by Schottky and Wagner. A good account will be found in Jost, *Diffusion u. chem. Reaktion in festen Stoffen* (Dresden, 1937). See also Schottky, *Zeit. Elektrochem.* 45, 33 (1939).

of a simple atomic or molecular lattice, in which there is only a single component, the atom or molecule associated with each lattice point. Since in general the component in such crystals is actually an atom or, in a metal, perhaps rather an atomic ion, we shall speak of the component simply as an atom, without thereby meaning to exclude atomic ions or molecules, which can behave in the same way.

The imperfections are formed by the removal of an atom from the lattice point to which it belongs and the insertion of this atom either on a new lattice point or in an interlattice position. The former change forms an imperfection, only if the lattice point left vacant is one in the body of the lattice. The latter always forms an imperfection. There are thus two sorts of imperfections to consider even in this simplest case: (*a*) an unoccupied lattice point in the body of the crystal; (*b*) an interlattice atom. The numbers of these two types of imperfections are practically entirely independent of each other. In any configuration of the actual crystal there will be a certain number of imperfections of each type, but in any configuration which is important to our calculations we shall assume that these numbers are small compared with the total number of atoms in the crystal. As a consequence of this we may assume further that all the imperfections are independent, and do not interact with one another. We shall use a notation which can be extended with the minimum of modification to the more complicated crystals to be considered in later sections.

It is important to start with a precise specification of some standard state of the crystal to which all changes can be unambiguously referred. We have already constructed partition functions for perfect crystals in Chapter IV, and it is therefore natural and convenient here to use as the standard state the *perfect crystal containing a given number of atoms* $N$. This standard crystal will have a partition function $K(T)$ $(=[\kappa(T)]^N)$, which can be constructed as in Chapter IV for any desired energy zero; we have here only to introduce the extra terms or factors that arise, when imperfections are taken into account. In doing this we shall make the approximation that any imperfection, caused by displacing an atom in the crystal, alters the energy of all quantum states of the crystal by a constant amount, but has no effect on the number or vibration frequencies of such states. Each distinguishable imperfect configuration will then possess the same partition function as the perfect crystal except for the constant change of energy. Referred to the original energy zero, however chosen, the new configuration will therefore have the partition function

$$K(T)\,e^{-W/kT},$$

where $W$ is the amount by which the energy of the new configuration, for

example, in its lowest quantum state, exceeds the energy of the standard perfect configuration in its corresponding state.

Let $N$ be the number of atoms present, $N^h$ the number of unoccupied lattice points (holes) in the body of the lattice, and $N^i$ the number of atoms in interlattice positions in any particular example of the crystal. The crystal is pure, and only atoms of type $A$ are present. The total number of lattice points available in the compact crystal will then be $N+N^h-N^i$ ($=N^l$ say). We shall denote the number of possible interlattice positions by $\alpha N$, where $\alpha$ is a constant, of the order of magnitude unity. Let $\zeta^h$ be the energy required to remove an atom from an internal lattice point to a new surface lattice point, leaving an unoccupied lattice point or hole. Let $\zeta^i$ be the energy required to take an atom from a surface lattice point to an interlattice position. Then, if the various imperfections do not interfere with one another, the extra energy of any configuration in the specified example, with $N^l$ lattice points in the compact crystal, $N^h$ holes and $N^i$ interlattice atoms, is

$$N^h\zeta^h + N^i\zeta^i. \qquad (1301, 1)$$

The total number of distinct configurations belonging to this example is

$$\frac{N^l!}{N^h!(N^l-N^h)!}\frac{(\alpha N^l)!}{N^i!(\alpha N^l-N^i)!} \quad (N^l=N+N^h-N^i). \qquad (1301, 2)$$

The first factor in (2) is the number of ways $N^h$ unoccupied lattice points can be chosen from a total of $N^l$; the second factor is the number of ways $N^i$ interlattice atoms can be placed on the available $\alpha N^l$ interlattice sites.

Since any degree of imperfection may be present, the complete partition function for the crystal with its actual imperfections will be $K(T)\,\Gamma(T)$, say, given by

$$K(T)\,\Gamma(T) = K(T)\,\Sigma_{N^h,N^i}\frac{N^l!}{N^h!(N^l-N^h)!}\frac{(\alpha N^l)!}{N^i!(\alpha N^l-N^i)!}e^{-(N^h\zeta^h+N^i\zeta^i)/kT}$$

$$(N^l=N+N^h-N^i). \qquad (1301, 3)$$

The result is obtained by summing $K(T)\,e^{-W/kT}$ over all possible configurations, perfect and imperfect. We repeat that $K(T)$ is the partition function for the perfect crystal of $N$ atoms. It is only the extra factor $\Gamma(T)$, hitherto neglected, which we require to study here.

It is not possible to sum the series for $\Gamma(T)$ in (3) in finite terms. We may, however, proceed by the commonly used method, which can be rigorously justified, of determining the maximum term in the series for $\Gamma(T)$ and replacing $\log\Gamma(T)$ by the logarithm of this maximum term. We recall that $N^l=N+N^h-N^i$, and that $N$ has a given fixed value. Substituting the

value of $N^l$ into (3), we have

$$\Gamma(T) = \Sigma_{N^h,N^i} \frac{(N+N^h-N^i)!}{N^h!(N-N^i)!} \frac{(\alpha N+\alpha N^h-\alpha N^i)!}{N^i!(\alpha N+\alpha N^h-[\alpha+1]N^i)!} e^{-(N^h\zeta^h+N^i\zeta^i)/kT}. \quad (1301,4)$$

The maximum term is then fixed by the equations

$$\frac{\partial}{\partial N^h}\log(\text{term}) = \log N^l-\log N^h+\alpha\log(\alpha N^l)-\alpha\log(\alpha N^l-N^i)-\zeta^h/kT = 0, \quad (1301,5)$$

$$\frac{\partial}{\partial N^i}\log(\text{term}) = -\log N^l+\log(N^l-N^h)-\alpha\log(\alpha N^l)-\log N^i + (\alpha+1)\log(\alpha N^l-N^i)-\zeta^i/kT = 0. \quad (1301,6)$$

These equations are sufficient to determine values $N^h_*$ and $N^i_*$ of $N^h$ and $N^i$, for which the terms of (3) assume their maximum value. When $\zeta^h/kT \gg 1$, $\zeta^i/kT \gg 1$, as will generally be the case in practice, $N^h_*/N \ll 1$ and $N^i_*/N \ll 1$, so that $N^l$ is effectively equal to $N$. Equations (5) and (6) then reduce to

$$N^h_*/N \simeq e^{-\zeta^h/kT}, \quad (1301,7)$$

$$N^i_*/\alpha N \simeq e^{-\zeta^i/kT}. \quad (1301,8)$$

These approximate relations can be obtained more simply by replacing $N^l$ by $N$ throughout formula (3) before performing the differentiations.

The average or equilibrium values $\overline{N^h}$ and $\overline{N^i}$ of $N^h$ and $N^i$ can as usual be shown to be given by the equations

$$\overline{N^h} = N^h_*, \quad \overline{N^i} = N^i_*, \quad (1301,9)$$

so that

$$\overline{N^h} = Ne^{-\zeta^h/kT}, \quad \overline{N^i} = \alpha Ne^{-\zeta^i/kT}. \quad (1301,10)$$

These equations determine the equilibrium degree of imperfection in this simple crystal. The numbers concerned are usually so small that they would be barely detectable by measurement of any equilibrium property; their presence in such a crystal, and in the similar more complicated cases which we proceed to discuss, is then indirectly inferred, as mentioned in § 1300, from properties of the crystal observable in various transport phenomena. These phenomena, however, are in general detectable only in more complicated crystals containing at least two different sorts of atom, and we therefore proceed to generalize these results to the simplest type of two-atom crystals such as an alkali halide or a silver halide.

**§ 1302. Lattice imperfections in crystalline salts, such as** NaCl, AgBr. In this section the components $A$, $B$ of the salt $AB$, or $A^+B^-$, are assumed to be present in exactly equal numbers. This restriction is relaxed in § 1303. Since the salts to which our formulae apply most directly are ionic, we shall write throughout in terms of the ions $A^+$ and $B^-$. All results are formally unaffected if we choose instead the neutral atoms $A$ and $B$

with a corresponding change of energy zero. We again take as standard state the perfect crystal $AB$ of a given number of molecules, for which we may suppose that we have constructed the partition function $K(T)$. We again assume that the states of any given imperfect configuration differ only by a constant energy from the corresponding states of the perfect configuration, so that they possess the partition function $K(T)\,e^{-W/kT}$.

Let $N$ $(=N_A, N_B)$ be the number of $AB$ molecules or $A^+$ or $B^-$ ions of either sort present; in any configuration let $N^l$ be the total number of all lattice points for $A$ or $B$ present in the compact crystal; there will then be $\frac{1}{2}N^l$ lattice points $A$ and $\frac{1}{2}N^l$ lattice points $B$; let $N_A^h$ and $N_B^h$ be the number of $A$ and $B$ lattice points unoccupied, and $N_A^i$ and $N_B^i$ the number of $A^+$ and $B^-$ ions in interlattice positions respectively. It can safely be assumed that an $A^+$ ion never occupies a $B^-$ site or vice versa. Then

$$\tfrac{1}{2}N^l = N_A + N_A^h - N_A^i, \quad \tfrac{1}{2}N^l = N_B + N_B^h - N_B^i. \qquad (1302,1)$$

Since $N_A = N_B = N$, we have

$$N_A^h - N_A^i = N_B^h - N_B^i, \qquad (1302,2)$$

but these $N$'s are otherwise unrestricted. We shall further assume that the number of interlattice points is $\alpha N^l$, where $\alpha$ is a constant, and that all these interlattice points are indifferently available for either $A^+$ or $B^-$ ions. For NaCl the lattice is simple cubic when the difference between Na and Cl is ignored, and $\alpha$ will be 1 if the interlattice positions are the cube centres. We define the energies $\zeta_A^h$, $\zeta_A^i$, for the $A^+$ ions, and the exactly similar energies $\zeta_B^h$, $\zeta_B^i$ for the $B^-$ ions, just as we defined the similar quantities $\zeta^h$, $\zeta^i$ in § 1301. Then if the various imperfections do not interfere with one another, the extra energy of the specified imperfect configuration is

$$N_A^h \zeta_A^h + N_A^i \zeta_A^i + N_B^h \zeta_B^h + N_B^i \zeta_B^i. \qquad (1302,3)$$

The total number of these equivalent configurations may be shown, by arguments similar to those establishing (1301, 3), to be

$$\frac{(\frac{1}{2}N^l)!}{N_A^h!(\frac{1}{2}N^l - N_A^h)!}\,\frac{(\frac{1}{2}N^l)!}{N_B^h!(\frac{1}{2}N^l - N_B^h)!}\,\frac{(\alpha N^l)!}{N_A^i!N_B^i!(\alpha N^l - N_A^i - N_B^i)!}. \qquad (1302,4)$$

Combining (3) and (4) we now find that the complete partition function for the crystal with any imperfections is $K(T)\,\Gamma(T)$, where

$$\Gamma(T) = \Sigma_{N_A^h, N_A^i, N_B^h, N_B^i} \frac{(\frac{1}{2}N^l)!}{N_A^h!(\frac{1}{2}N^l - N_A^h)!}\,\frac{(\frac{1}{2}N^l)!}{N_B^h!(\frac{1}{2}N^l - N_B^h)!} \times \frac{(\alpha N^l)!}{N_A^i!N_B^i!(\alpha N^l - N_A^i - N_B^i)!}\, e^{-[N_A^h\zeta_A^h + N_A^i\zeta_A^i + N_B^h\zeta_B^h + N_B^i\zeta_B^i]/kT}. \qquad (1302,5)$$

The summation is here restricted by the conditions (1).

We may now proceed to evaluate $\log \Gamma(T)$ in the usual way by equating it to log(max. term) in the summation in (5). The maximum term is determined by satisfying

$$\left[-\frac{\zeta_A^h}{kT}+\log\frac{\frac{1}{2}N^l-N_A^h}{N_A^h}\right]dN_A^h+\left[-\frac{\zeta_B^h}{kT}+\log\frac{\frac{1}{2}N^l-N_B^h}{N_B^h}\right]dN_B^h$$
$$+\left[-\frac{\zeta_A^i}{kT}+\log\frac{\alpha N^l-N_A^i-N_B^i}{N_A^i}\right]dN_A^i+\left[-\frac{\zeta_B^i}{kT}+\log\frac{\alpha N^l-N_A^i-N_B^i}{N_B^i}\right]dN_B^i$$
$$+\left[\tfrac{1}{2}\log\frac{\frac{1}{2}N^l}{\frac{1}{2}N^l-N_A^h}+\tfrac{1}{2}\log\frac{\frac{1}{2}N^l}{\frac{1}{2}N^l-N_B^h}+\alpha\log\frac{\alpha N^l}{\alpha N^l-N_A^i-N_B^i}\right]dN^l=0, \quad (1302,6)$$

subject to the conditions

$$\tfrac{1}{2}dN^l = dN_A^h-dN_A^i = dN_B^h-dN_B^i. \quad (1302,7)$$

If we assume that the important values of $N_A^h$, $N_A^i$, $N_B^h$, $N_B^i$ are all small compared with $\frac{1}{2}N^l$, which is then equivalent to $N$, equations (6) and (7) can be reduced to the simple approximate form

$$\left[-\frac{\zeta_A^h}{kT}+\log\frac{N}{N_A^h}\right]dN_A^h+\left[-\frac{\zeta_B^h}{kT}+\log\frac{N}{N_B^h}\right]dN_B^h+\left[-\frac{\zeta_A^i}{kT}+\log\frac{2\alpha N}{N_A^i}\right]dN_A^i$$
$$+\left[-\frac{\zeta_B^i}{kT}+\log\frac{2\alpha N}{N_B^i}\right]dN_B^i=0, \quad (1302,8)$$

subject to the restriction

$$dN_A^h-dN_A^i = dN_B^h-dN_B^i. \quad (1302,9)$$

From these equations we deduce (by Lagrange's method) that the values $N_A^{h*}, \ldots$ of $N_A^h, \ldots$, yielding the maximum term in $\Gamma(T)$, are given by

$$\frac{N_A^{h*}}{N}=\frac{1}{Q}e^{-\zeta_A^h/kT}, \quad \frac{N_B^{h*}}{N}=Qe^{-\zeta_B^h/kT}, \quad (1302,10)$$

$$\frac{N_A^{i*}}{2\alpha N}=Qe^{-\zeta_A^i/kT}, \quad \frac{N_B^{i*}}{2\alpha N}=\frac{1}{Q}e^{-\zeta_B^i/kT}, \quad (1302,11)$$

where $Q$ has to be adjusted to satisfy (2). The roots of these equations give also the equilibrium values $\overline{N_A^h}, \ldots$ of $N_A^h, \ldots$.

The solution of equations (2), (10) and (11) gives rise to various different limiting cases of interest. By substituting from (10) and (11) into (2), we find for $Q$ the equation

$$\frac{1}{Q}(e^{-\zeta_A^h/kT}+2\alpha e^{-\zeta_B^i/kT}) = Q(e^{-\zeta_B^h/kT}+2\alpha e^{-\zeta_A^i/kT}), \quad (1302,12)$$

from which it follows that

$$Q^2 = e^{-(\zeta_A^h-\zeta_B^h)/kT}\left\{\frac{1+2\alpha e^{-(\zeta_B^i-\zeta_A^h)/kT}}{1+2\alpha e^{-(\zeta_A^i-\zeta_B^h)/kT}}\right\}. \quad (1302,13)$$

It is now convenient to introduce the notation

$$K = e^{-(\zeta_A{}^h+\zeta_B{}^h)/kT}, \quad k_A = 2\alpha e^{-(\zeta_A{}^i-\zeta_B{}^h)/kT}, \quad k_B = 2\alpha e^{-(\zeta_B{}^i-\zeta_A{}^h)/kT}. \quad (1302, 14)$$

In terms of these quantities

$$\frac{\overline{N_A^h}}{N} = K^{\frac{1}{2}}\left(\frac{1+k_A}{1+k_B}\right)^{\frac{1}{2}}, \quad \frac{\overline{N_B^h}}{N} = K^{\frac{1}{2}}\left(\frac{1+k_B}{1+k_A}\right)^{\frac{1}{2}}, \quad (1302, 15)$$

$$\frac{\overline{N_A^i}}{N} = k_A K^{\frac{1}{2}}\left(\frac{1+k_B}{1+k_A}\right)^{\frac{1}{2}}, \quad \frac{\overline{N_B^i}}{N} = k_B K^{\frac{1}{2}}\left(\frac{1+k_A}{1+k_B}\right)^{\frac{1}{2}}. \quad (1302, 16)$$

The equilibrium concentrations of holes and interlattice atoms are thus given simply in terms of $K$, $k_A$, $k_B$. The factor $K$ contains the energy $\zeta_A^h + \zeta_B^h$, which is that required to take a pair of ions (a molecule) out of the lattice and place them correctly on new surface lattice points. The factor $k_A$ contains the energy $\zeta_A^i - \zeta_B^h$, which is that required to take a pair of ions from surface lattice points (leaving no holes), put the $A^+$ in an interlattice position, and the $B^-$ back in an existing hole in the lattice at a $B$ lattice point. Similarly the factor $k_B$ contains the energy $\zeta_B^i - \zeta_A^h$, which is that necessary to take a pair of ions from surface lattice points (leaving no holes), put the $B^-$ in an interlattice position, and the $A^+$ back into an existing hole in the lattice at an $A$ lattice point.

The factors $k_A$, $k_B$ can well be of any magnitude relative to unity in different cases. In the actual cases of most alkali halides or silver halides, the $A^+$ is a very small ion compared with the $B^-$, so that one would expect $\zeta_B^i$, the energy required to place $B^-$ in an interlattice position, to be considerably larger than any of the other $\zeta$'s. The energy $\zeta_A^i$ required to place $A^+$ in an interlattice position might well be either larger or smaller than $\zeta_A^h$ or $\zeta_B^h$, which might be nearly equal. In such circumstances at ordinary temperatures $k_B \ll 1$, while $k_A$ may be either very large or very small, or have any intermediate value. It appears to be the case that $k_A \gg 1$ for AgBr, and $k_A \ll 1$ for NaCl. Formulae (15) and (16) simplify in the manner shown in Table 1 in the various limiting cases.

TABLE 1

*Dominant terms in the equilibrium concentrations of holes and interlattice atoms. The entries in heavy type are themselves large compared with the others in the same row*

| | $k_A$ | $k_B$ | $\overline{N_A^h}/NK^{\frac{1}{2}}$ | $\overline{N_B^h}/NK^{\frac{1}{2}}$ | $N_A^i/NK^{\frac{1}{2}}$ | $N_B^i/NK^{\frac{1}{2}}$ | Example |
|---|---|---|---|---|---|---|---|
| 1 | $\gg 1$ | $\ll 1$ | $\mathbf{k_A^{\frac{1}{2}}}$ | $1/k_A^{\frac{1}{2}}$ | $\mathbf{k_A^{\frac{1}{2}}}$ | $k_B k_A^{\frac{1}{2}}$ | AgBr |
| 2 | $\ll 1$ | $\gg 1$ | $1/k_B^{\frac{1}{2}}$ | $\mathbf{k_B^{\frac{1}{2}}}$ | $k_A k_B^{\frac{1}{2}}$ | $\mathbf{k_B^{\frac{1}{2}}}$ | -- |
| 3 | $\gg 1$ | $\gg 1$ | $(k_A/k_B)^{\frac{1}{2}}$ | $(k_B/k_A)^{\frac{1}{2}}$ | $(\mathbf{k_A k_B})^{\frac{1}{2}}$ | $(\mathbf{k_A k_B})^{\frac{1}{2}}$ | — |
| 4 | $\ll 1$ | $\ll 1$ | **1** | **1** | $k_A$ | $k_B$ | NaCl |

*Case* 1. Effectively all the imperfections are holes at the $A$ lattice points, balanced by equal numbers of interlattice ions $A^+$.

$$\overline{N_A^h} = \overline{N_A^i} = N(2\alpha)^{\frac{1}{2}} e^{-\frac{1}{2}(\zeta_A{}^h+\zeta_A{}^i)/kT}. \qquad (1302, 17)$$

This formula and other simplified formulae can naturally be obtained more simply by constructing a $\Gamma(T)$ in which only the ultimately important imperfections are allowed for.

*Case* 2. Exactly similar to Case 1 with subscripts $A$ and $B$ interchanged.

*Case* 3. Effectively all the imperfections are interlattice ions, equal numbers of each sort being present;

$$\overline{N_A^i} = \overline{N_B^i} = N2\alpha\, e^{-\frac{1}{2}(\zeta_A{}^i+\zeta_B{}^i)/kT}. \qquad (1302, 18)$$

*Case* 4. Effectively all the imperfections are holes in the lattice, equal numbers of each sort being present;

$$\overline{N_A^h} = \overline{N_B^h} = Ne^{-\frac{1}{2}(\zeta_A{}^h+\zeta_B{}^h)/kT}. \qquad (1302, 19)$$

The basic assumption of our calculation, that all the ratios $\overline{N_A^h}/N, \ldots$ are small compared with unity, will be satisfied in the various cases provided the various exponents such as $\frac{1}{2}(\zeta_A^h + \zeta_A^i)/kT$ are large compared with unity.

Lattice imperfections, whether holes or interlattice atoms, endow the corresponding ions with mobility—the power to move through the crystal under the influence of a concentration gradient or an applied electric field. Consider for definiteness an interlattice atom. An interlattice atom in its lowest state is still unable to leave its place which is one of equilibrium locally. But a certain fraction of interlattice atoms will have an excess energy sufficient to enable them to pass to similar neighbouring interlattice points and the effective mobility of the ions will be proportional to the number of such atoms. Without attempting any precise theory, it is sufficient to note here that the fraction of interlattice atoms with excess energy will be approximately proportional to a function of the form $e^{-\epsilon^*/kT}$ where $\epsilon^*$ is an activation energy, while according to the formulae of this section $\overline{N_A^i}$ is itself proportional to $e^{-\zeta/kT}$, where $\zeta$ is one of the combinations found in equations (17)–(19). Thus the important factor in the mobility in any of our special cases is of the form

$$e^{-(\zeta+\epsilon^*)/kT}. \qquad (1302, 20)$$

Any more accurate formulation than this really requires a proper consideration of transport phenomena, and lies outside the range of this book.

**§ 1303. Presence of excess of one component in a binary salt.** If one of the components, $A$ say, is present in small excess in a salt $AB$, a large number of special cases arise which can be simply treated by an extension of the analysis of § 1302. Such assemblies are not without importance. For example AgBr may contain an excess of free silver, with a marked

influence on its properties. We shall content ourselves with the discussion of one particular case, sufficient to illustrate the methods required for the whole family of cases, which arise when one considers different dominant forms of imperfection in the crystal of the pure binary salt and different ways of fitting in the extra atoms.

We shall discuss the following case:

*A salt $AB$ whose only imperfections frequent enough to matter are holes at the $A$ lattice points and interlattice $A^+$ ions.* The presence of extra $A$ atoms in the lattice is to be allowed for; they will enter as $A^+$ ions either in the hitherto vacant holes at $A$ lattice points or as further interlattice $A^+$ ions. The corresponding number of electrons must also be accommodated, but we shall not consider these explicitly; we shall assume that they are suitably accommodated in some manner which does not give rise to any significant extra factor in the partition function. If they were accommodated in fixed locations distributed freely through the lattice, important extra factors would have to be introduced.

We must again start by specifying carefully the standard state of the assembly, relative to which all other configurations will be described. This standard state we shall again take to be the perfect crystal of a given number $N$ of molecules $AB$ and partition function $K(T)$. Its imperfections, which are assumed to be holes at $A$ lattice points and interlattice $A^+$ ions, are as described in the foregoing sections. There are now present in addition in the assembly $A$ atoms, either free or absorbed by the crystal $AB$, where they form extra imperfections. We shall take the standard state for all the extra $A$ atoms to be that of rest at infinite dispersion. Extra imperfections in the crystal can now be formed by inserting free $A$ atoms, so that $N_A^h$ and $N_A^i$ are no longer equal but are entirely independent. We may suppose that the energy of an $A$ atom, when it has been added to the crystal as an interlattice ion in its lowest state and an electron, is $-\chi_A^i$ above (or $\chi_A^i$ below) that of the standard state, and that it contributes a factor $q_A(T)$ to the partition function for the normal modes of the crystal, whose partition function is otherwise unaffected. In any given configuration with $N_A^h$ holes and $N_A^i$ interlattice $A^+$ ions the crystal will have absorbed $N_A^i - N_A^h$ free $A$ atoms, and its partition function will therefore be

$$K(T)\, e^{-N_A^h(\zeta_A^h+\zeta_A^i)/kT}\, [q_A(T)\, e^{\chi_A^i/kT}]^{N_A^i-N_A^h}. \tag{1303, 1}$$

Since the $B^-$ ions are here all on their lattice points, the number of lattice points in the compact crystal is fixed at $2N_B$, and the number of configurations with given $N_A^h$, $N_A^i$ is

$$\frac{N_B!}{N_A^h!(N_B-N_A^h)!}\,\frac{(2\alpha N_B)!}{N_A^i!(2\alpha N_B-N_A^i)!}. \tag{1303, 2}$$

Hitherto in this chapter we have been working with assemblies or phases of a fixed number of systems, and it has been natural to use ordinary partition functions. Here we are interested in a phase, the crystal, in which the number of $B$'s is fixed, but the number of $A$'s can vary. It is convenient to construct and use a grand partition function, or more strictly a semi-grand one, in terms of the variables $T$, $V$, $N_B$ and $\lambda_A$, where $\lambda_A$ is the absolute activity of the free $A$ atoms. Using (1) and (2), we may write this

$$K(T)\,\Gamma(T,\lambda_A,N_B),$$

where $\Gamma(T,\lambda_A,N_B)$ is given by

$$\Gamma(T,\lambda_A,N_B) = \Sigma_{N_A{}^h,\,N_A{}^i}\,[\lambda_A q_A(T)]^{N_A{}^i-N_A{}^h}\,\frac{N!}{N_A^h!(N-N_A^h)!}\,\frac{(2\alpha N)!}{N_A^i!(2\alpha N-N_A^i)!}$$
$$\times\, e^{-[N_A{}^h(\zeta_A{}^h+\zeta_A{}^i)-(N_A{}^i-N_A{}^h)\chi_A{}^i]/kT}. \qquad (1303,3)$$

The double summation is here unrestricted. The grand partition function factor $\Gamma(T,\lambda_A,N_B)$ may be evaluated as usual by searching for the maximum term. This may be shown to occur for the values $N_A^{h*}$, $N_A^{i*}$, given by

$$N_A^{h*} = N e^{-(\zeta_A{}^h+\zeta_A{}^i)/kT}/\{\lambda_A q_A(T)\,e^{\chi_A{}^i/kT}\}, \qquad (1303,4)$$

$$N_A^{i*} = 2\alpha N\lambda_A q_A(T)\,e^{\chi_A{}^i/kT}. \qquad (1303,5)$$

These values are, as usual, also the equilibrium values $\overline{N_A^h}$, $\overline{N_A^i}$ of $N_A^h$, $N_A^i$.

We observe that

$$\overline{N_A^h}\,\overline{N_A^i} = 2\alpha N^2 e^{-(\zeta_A{}^h+\zeta_A{}^i)/kT} = \overline{N_0}^2, \qquad (1303,6)$$

where $\overline{N_0}$ denotes the equilibrium value of $N_A^h$ and of $N_A^i$ when no extra $A$ is present, so that $N_A^h = N_A^i$. If we denote the excess (positive or negative) of $A$ atoms by $\Delta N_A$, we must have

$$\overline{N_A^i} - \overline{N_A^h} = \overline{\Delta N_A}. \qquad (1303,7)$$

Solving the simultaneous equations (6) and (7) for $\overline{N_A^h}$ and $\overline{N_A^i}$, we obtain

$$\overline{N_A^h} = [\overline{N_0}^2 + (\tfrac{1}{2}\overline{\Delta N_A})^2]^{\frac{1}{2}} - \tfrac{1}{2}\overline{\Delta N_A}, \qquad (1308,8)$$

$$\overline{N_A^i} = [\overline{N_0}^2 + (\tfrac{1}{2}\overline{\Delta N_A})^2]^{\frac{1}{2}} + \tfrac{1}{2}\overline{\Delta N_A}. \qquad (1303,9)$$

Formulae (8) and (9) give the equilibrium state of the crystal for given excess $\Delta N_A$ (positive or negative) of $A$. If, however, the crystal is in equilibrium with another phase of given $\lambda_A$ which controls the excess of $A$, it is more useful to use formulae (4) and (5).

There are obviously many other such cases which can be discussed in similar ways. We need not investigate these, as they conform closely to the same model, and give results of similar form. In any particular case an investigation similar to that given here will yield the results required. If a large variety of special cases need discussion, it may be more convenient to

proceed by constructing the complete grand partition function with all types of imperfection. This is formulated for reference but not developed in the following section.

**§ 1304. Generalization of imperfect crystals.** We shall now consider very briefly a crystal $AB$ with a small excess or deficiency of $A$ when there are $B$ holes as well as $A$ holes and interlattice $B$ atoms as well as interlattice $A$ atoms. For this case it is most convenient to choose as independent variables the absolute activities $\lambda_A$ and $\lambda_B$ of both kinds of atoms and to construct the completely grand partition function $\Xi(T, \lambda_A, \lambda_B)$. We take the energy zeros of $A$ atoms and $B$ atoms to be their lowest states at infinite dispersion and assume as an approximation that every $A$ atom (or $B$ atom) makes the same contribution to the normal modes, whether it is on a lattice point or an interlattice atom. It is assumed that there are $2N$ lattice points in all in the compact crystal. We then have

$$\begin{aligned}\Xi(T, \lambda_A, \lambda_B) = \Sigma_{N_A{}^h, N_A{}^i} & \frac{N!}{N_A^h!(N-N_A^h)!}\,\frac{(2\alpha N)!}{N_A^i!(2\alpha N - N_A^i)!} \\ & \times [\lambda_A \kappa_A(T)]^{N-N_A{}^h+N_A{}^i}\, e^{-(N_A{}^h\zeta_A{}^h + N_A{}^i\zeta_A{}^i)/kT} \\ & \times \Sigma_{N_B{}^h, N_B{}^i} \frac{N!}{N_B^h!(N-N_B^h)!}\,\frac{(2\alpha N)!}{N_B^i!(2\alpha N - N_B^i)!} \\ & \times [\lambda_B \kappa_B(T)]^{N-N_B{}^h+N_B{}^i}\, e^{-(N_B{}^h\zeta_B{}^h + N_B{}^i\zeta_B{}^i)/kT}. \qquad (1304, 1)\end{aligned}$$

We may as usual replace $\Xi$ by its dominant term $\Xi^*$ determined by the equations

$$\partial\Xi^*/\partial N_A^h = 0, \quad \partial\Xi^*/\partial N_A^i = 0, \qquad (1304, 2)$$

$$\partial\Xi^*/\partial N_B^h = 0, \quad \partial\Xi^*/\partial N_B^i = 0. \qquad (1304, 3)$$

The equilibrium values $\overline{N_A^h}$, $\overline{N_A^i}$, $\overline{N_B^h}$, $\overline{N_B^i}$ of $N_A^h$, $N_A^i$, ... are then the values of $N_A^h$, $N_A^i$, ... occurring in the dominant term $\Xi^*$. The general relations

$$\overline{N_A} = \lambda_A \frac{\partial}{\partial \lambda_A} \Xi, \quad \overline{N_B} = \lambda_B \frac{\partial}{\partial \lambda_B} \Xi \qquad (1304, 4)$$

thus lead to the physically obvious result

$$\overline{N_A} = N - \overline{N_A^h} + \overline{N_A^i}, \quad \overline{N_B} = N - \overline{N_B^h} + \overline{N_B^i}. \qquad (1304, 5)$$

We shall not pursue any further the development of these formulae which we have included merely to illustrate the power and generality of this method of procedure.

**§ 1305. Ideal solutions of impurities.** The discussion in § 1303 leads us to investigate the properties of crystals which may be assumed to be without imperfections, except that they contain small quantities of foreign

atoms as impurities. We could, if we wished, investigate by the present methods the simultaneous effects of ordinary lattice imperfections and foreign atoms, but we shall not go into such detail. The construction of thermodynamic functions for crystals containing small amounts of impurity is extremely similar to the construction for liquids, which we have already given in § 822. It will therefore be unnecessary to go into great detail. One can, however, be rather more precise for crystals than for liquids.

Atoms of the impurity $B$ can be inserted in the lattice of $A$ in general either by substitution on the $A$ lattice points or as interlattice atoms. One can discuss both cases together, though in any particular case one would expect one or other type to dominate. Consider a crystal of $N$ atoms $A$, neglecting imperfections, in equilibrium with $B$ atoms of absolute activity $\lambda_B$. In any particular configuration let there be $N_B^l$ atoms $B$ on $A$ lattice points, and $N_B^i$ interlattice $B$ atoms. The total number $N^l$ of lattice points is then $N+N_B^l$, and the total number of such configurations

$$\frac{N^l!}{N_B^l!\,N!}\,\frac{(\alpha N^l)!}{N_B^i!(\alpha N^l-N_B^i)!}. \qquad (1305,1)$$

The standard state of the assembly is taken to be the perfect pure $A$ crystal and free atoms $B$, dispersed, in their lowest states. The extra energy of the above configurations with absorbed $B$ atoms, assumed sparse and therefore independent, is then

$$N_B^l w_B^l + N_B^i w_B^i. \qquad (1305,2)$$

Here $w_B^l$ is the energy required to remove an $A$ atom from a lattice point leaving a hole and then to insert the $A$ on a new (surface) lattice point and a $B$ in the hole so left; $w_B^i$ is the energy required to insert a $B$ in an interlattice position. The extra vibrational factor in the crystal partition function for a $B$ atom in either position may be taken to be $q_B(T)$. Then the extra configurational grand partition function factor for this crystal is

$$\Gamma(T,\lambda_B) = \Sigma_{N_B{}^l,N_B{}^i}\frac{N^l!}{N_B^l!\,N!}\,\frac{(\alpha N^l)!}{N_B^i!(\alpha N^l-N_B^i)!}\,e^{-(N_B{}^l w_B{}^l+N_B{}^i w_B{}^i)/kT} \times [\lambda_B q_B(T)]^{N_B{}^l+N_B{}^i}. \qquad (1305,3)$$

This may be treated in the usual way. The equilibrium values of $N_B^l$ and $N_B^i$ are given by the equations

$$\overline{N_B^l}/N = \lambda_B q_B(T)\,e^{-w_B{}^l/kT}, \qquad (1305,4)$$

$$\overline{N_B^i}/\alpha N = \lambda_B q_B(T)\,e^{-w_B{}^i/kT}. \qquad (1305,5)$$

The two sorts of absorbed impurities are thus independent of each other to this approximation, which requires that

$$\overline{N_B^l}/N \ll 1, \quad \overline{N_B^i}/N \ll 1.$$

**§ 1306. Solubility of hydrogen in metals. General review.** The solubility of hydrogen in a number of metals has been studied experimentally, especially by Sieverts.* Most of these measurements are not of high accuracy, owing to the difficulty of ensuring the attainment of equilibrium, but they are sufficient to establish the general behaviour at least semi-quantitatively of the various metal-hydrogen assemblies.

The absorption of hydrogen by all the metals studied is found to be proportional to the square root of the hydrogen pressure for small amounts absorbed, that is to say for low pressures or for high temperatures. The obvious explanation is that the hydrogen is absorbed as H atoms. With respect to the state of the absorbed H atoms, the metals fall naturally into two sharply divided groups which we may conveniently call poor absorbers and good absorbers.†

In the poor absorbers, of which copper, iron, cobalt, nickel are typical examples, the amount of hydrogen increases as the temperature increases. In these metals the crystal lattice is completely unaffected by dissolved hydrogen, even when it is present in appreciable concentrations. We may then most reasonably picture the hydrogen as unattached to particular metal atoms. Further, in view of the fact that we must expect the hydrogen atom not to retain its electron in the metal, but rather to be present as a proton, the electron joining the general body of conduction electrons, we can hardly expect the proton to be attached to any particular location in the metal at all. We may here rather think of it as free to wander through the whole, or a substantial fraction of the interior of the metal.

These conditions lead us to a model which is the exact three-dimensional analogue of mobile monolayers discussed in § 1003. We can reasonably refer to the H atoms absorbed by the poor absorbers as mobile. This discussion is continued in more detail in § 1307.

The good absorbers, of which thorium, titanium, vanadium are examples, absorb between $10^3$ and $10^5$ times as much hydrogen as the poor absorbers at the same temperature, and the amount absorbed decreases as the temperature is increased. The proportionality of the amount absorbed to the square root of the pressure holds only at high temperatures; at lower temperatures as the pressure is increased a saturation limit is approached. In these metals we are led to suppose that the H atoms are tightly bound to the metal atoms. We assume that each metal atom can bind $\alpha$ H atoms, where $\alpha$ is a small integer. We can then apply the theory of § 1305 slightly modified, and we shall do so in § 1308. This model is closely analogous to that of ideal localized monolayers discussed in § 1004, and we therefore refer to it

* Detailed references will be given later.

† Fowler and Smithells, *Proc. Roy. Soc.* A, **160**, 37 (1937).

as an ideal localized assembly of absorbed H atoms. We shall find this model adequate for the metals Zr, Th, but not for Ti, and notably not for Pd. For these two metals one is compelled to take account of the mutual interaction of the absorbed H atoms and are so led to the model of a regular localized assembly, closely analogous to that used in §§ 1006–1012 for monolayers. We shall discuss this model and its application to palladium in §§ 1309–1310.

**§ 1307. Ideal mobile assembly of H atoms in poor absorbers.** As explained in § 1306 we assume the hydrogen in the poor absorbers to be present in the metal as a gas of protons free to move in a uniform potential energy $w_H$, relative to the state of infinite dispersion of H atoms, over a volume $V_H$ either equal to or at least comparable with the volume $V$ of the metal. The necessary modification of (1305, 3) is

$$\Gamma(T, \lambda_H) = \Sigma_{N_H} \frac{1}{N_H!}\{\lambda_H l_H(T) \rho\}^{N_H} e^{-N_H w_H/kT} = \exp\{\lambda_H l_H(T) \rho e^{-w_H/kT}\}, \tag{1307, 1}$$

where $\rho$ is the nuclear spin weight and $l_H(T)$ is the contribution of the translational kinetic energy of a free proton to the partition function, given by

$$l_H(T) = \frac{(2\pi m_H kT)^{\frac{3}{2}}}{h^3} V_H. \tag{1307, 2}$$

The equilibrium value of $N_H$ is therefore given by

$$\overline{N_H} = \lambda_H l_H(T) \rho e^{-w_H/kT}, \tag{1307. 3}$$

the familiar formula for a perfect gas in an enclosure of volume $V_H$ and uniform potential energy $w_H$. The absolute activity $\lambda_H$ in a gas consisting almost entirely of diatomic molecules $H_2$ at a pressure $p$ is given by

$$\lambda_H = \lambda_{H_2}^{\frac{1}{2}} = \left(\frac{p}{kT}\right)^{\frac{1}{2}} e^{-\frac{1}{2}\chi_d/kT} \left\{\frac{(2\pi 2 m_H kT)^{\frac{3}{2}}}{h^3} \frac{8\pi^2 A kT}{h^2} \frac{\rho^2}{2}\right\}^{-\frac{1}{2}}, \tag{1307, 4}$$

where $\chi_d$ is the energy required to dissociate an $H_2$ molecule in its lowest state into two free H atoms in their lowest states, and $A$ is the moment of inertia of the $H_2$ molecule. Combining (3) with (4), we obtain

$$\frac{\overline{N_H}}{V_H} = \left(\frac{m_H^3}{16\pi A^2 h^2 kT}\right)^{\frac{1}{2}} p^{\frac{1}{2}} e^{-(w_H + \frac{1}{2}\chi_d)/kT}. \tag{1307, 5}$$

On inserting numerical values, we find for the solubility $s$ of hydrogen in the metal

$$\frac{s}{s^\dagger} = 1{\cdot}6 \times 10^4 \frac{V_H}{V} \frac{(p/P^\dagger)^{\frac{1}{2}}}{\rho_m T^{\frac{1}{2}}} e^{-(w_H + \frac{1}{2}\chi_d)/kT}, \tag{1307, 6}$$

where $\rho_m$ is the density of the metal in g./cm.$^3$, $P^\dagger$ denotes an atmosphere and $s^\dagger$ a solubility of 1 cm.$^3$ gas at S.T.P. per 100 g. metal. For comparison with

solubility measurements at 1 atmosphere and temperatures around 1000° K. for metals of the iron group ($\rho_m \simeq 8$) this reduces to

$$\log_e \frac{s}{s^\dagger} = 5{\cdot}9 + \log_e \frac{V_{\rm H}}{V} - \frac{w_{\rm H} + \frac{1}{2}\chi_d}{kT}. \qquad (1307, 7)$$

This formula is compared with the experimental data in Fig. 1. By extrapolation of the experimental lines we obtain as estimates of $V_{\rm H}/V$ the value

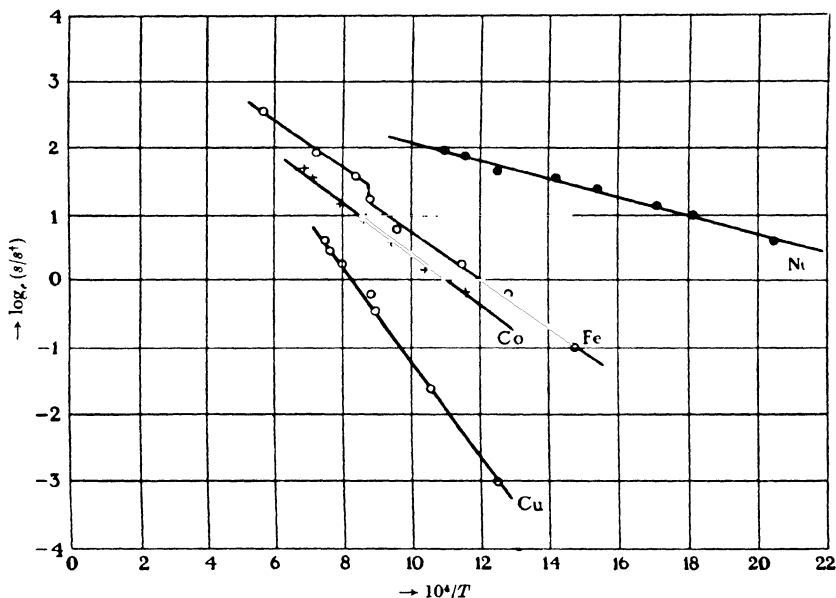



Fig. 1. Observed solubilities $s$ of hydrogen in various metals subjected to one atmosphere pressure of $H_2$, shown by plotting $\log_e (s/s^\dagger)$ against $10^4/T$, where $s^\dagger$ denotes 1 cm.$^3$ of $H_2$ at S.T.P. per 100 g. metal.
For sources see Fowler and Smithells, *Proc. Roy. Soc.* A, **160**, 37 (1937).

unity for copper and values between 1/4 and 1/10 for the metals of the iron group. Owing to the positive value of $w_{\rm H} + \frac{1}{2}\chi_d$ the solubility is always small.

**§ 1308. Ideal assembly of localized H atoms in good absorbers.** In discussing the good absorbers of hydrogen we shall ignore the change of crystal forms produced by the absorption, and shall assume that the absorbed H atoms become strongly attached to the metal atoms without affecting their positions. We assume that each metal atom can bind $\alpha$ H atoms, where $\alpha$ is a small integer. In a crystal of $N$ metal atoms there are

then $\alpha N$ sites available for H atoms. For the contribution of the H atoms to the grand partition function we have then

$$\Gamma(T,\lambda_{\mathrm{H}}) = \Sigma_{N_{\mathrm{H}}} \frac{(\alpha N)!}{N_{\mathrm{H}}!(\alpha N - N_{\mathrm{H}})!} e^{-N_{\mathrm{H}} w_{\mathrm{H}}^{i}/kT} \{\lambda_{\mathrm{H}} q_{\mathrm{H}}(T)\rho\}^{N_{\mathrm{H}}}$$
$$= \{1 + \lambda_{\mathrm{H}} q_{\mathrm{H}}(T)\rho\, e^{-w_{\mathrm{H}}^{i}/kT}\}^{\alpha N}, \qquad (1308, 1)$$

where $w_{\mathrm{H}}^{i}$ is the energy required to change a free hydrogen atom in its lowest state to a bound atom in the metal in its lowest state, and $q(T)$ is the contribution of a bound hydrogen atom to the partition function due to its vibrations relative to the metal atom. The equilibrium number of absorbed H atoms is then

$$\overline{N}_{\mathrm{H}} = \lambda_{\mathrm{H}} \frac{\partial}{\partial \lambda_{\mathrm{H}}} \{\log \Gamma(T,\lambda_{\mathrm{H}})\} = \alpha N \frac{\lambda_{\mathrm{H}} q_{\mathrm{H}}(T)\rho\, e^{-w_{\mathrm{H}}^{i}/kT}}{1+\lambda_{\mathrm{H}} q_{\mathrm{H}}(T)\rho\, e^{-w_{\mathrm{H}}^{i}/kT}}. \qquad (1308, 2)$$

This formula could have been written down at once as the analogue of Langmuir's adsorption formula, since the physical assumptions in this treatment of absorption are exactly analogous to those in Langmuir's treatment of adsorption. If $s$ is the solubility of hydrogen and $s^*$ its saturation value, corresponding to $N_{\mathrm{H}} = \alpha N$, then

$$\frac{s}{s^* - s} = \frac{\overline{N}_{\mathrm{H}}}{\alpha N - \overline{N}_{\mathrm{H}}} = \lambda_{\mathrm{H}} q_{\mathrm{H}}(T)\rho\, e^{-w_{\mathrm{H}}^{i}/kT}. \qquad (1308, 3)$$

Substituting into (3) the value of $\lambda_{\mathrm{H}}$ in a gas of $H_2$ molecules given by (1307, 4) and inserting numerical values, we find

$$\frac{s}{s^* - s} = 48(p/P^\dagger)^{\frac{1}{2}}\, T^{-\frac{3}{4}} q_{\mathrm{H}}(T)\, e^{-w_{\mathrm{H}}^{i}/kT}, \qquad (1308, 4)$$

where $P^\dagger$ denotes one atmosphere. As a reasonable approximation we may take $q_{\mathrm{H}}(T)$ to be unity at the relevant temperatures. Using an average value of 700 for $T$ in the non-exponential factor, we have then

$$\frac{s}{s^* - s} \simeq 5 \times 10^{-4} (p/P^\dagger)^{\frac{1}{2}}\, e^{-(w_{\mathrm{H}}^{i} + \frac{1}{2}\chi_d)/kT}. \qquad (1308, 5)$$

We have already mentioned the difficulty of ensuring the attainment of equilibrium in the experimental study of absorption of hydrogen by metals, and an accurate test of formula (5) is not possible with the data available. It can be said, however, that the formula gives at least a semi-quantitative description of the data‡ for zirconium and thorium. For both metals the solubility decreases as the temperature increases, so that $w_{\mathrm{H}} + \frac{1}{2}\chi_d$ must be negative, the hydrogen having less energy as absorbed atoms than as gaseous molecules. For zirconium at 1100° C. the absorption is small and

‡ Sieverts and Roell, *Zeit. Anorg. Chem.* **153**, 289 (1926).

proportional to $p^{\frac{1}{2}}$. At 800° C. the absorption increases more slowly than $p^{\frac{1}{2}}$ and approaches a saturation value which is at least not far from $\alpha = 2$, indicating the formation of $ZrH_2$ molecules. At temperatures below 700° C. equilibrium is approached too slowly for the measurement to be useful for comparison with equilibrium theory. For thorium the data at 800° C. indicate saturation corresponding to the molecule $ThH_3$. On the other hand formula (5) is in disagreement with the experimental data* for vanadium, since for this metal the saturation decreases by a factor of about ten as the temperature is increased from 400 to 800° C., whereas our model requires a saturation value strictly independent of temperature. If the experimental data are reliable, it means that $\alpha$ increases as the temperature decreases.

**§ 1309. Solubility of hydrogen in palladium. Theory.** In the preceding section we have ignored any interactions between absorbed hydrogen atoms, because the experimental data are not sufficiently accurate to detect the presence of such interactions. The experimental data for the solubility of hydrogen in palladium being considerably more extensive and accurate call for a more exact theory. We therefore treat the assembly of hydrogen atoms in palladium as a regular assembly precisely analogous to regular monolayers discussed in §§ 1006–1012, and only slight modification of the formulae of these sections is required.

Strictly one should use the formulae of § 1012 suitably modified. As a matter of fact these formulae were originally derived by Lacher† for the palladium-hydrogen assembly. The less accurate formulae of §§ 1007–1008, suitably modified, are, however, adequate for comparison with the experimental data and for the sake of simplicity we shall use these. We therefore start with formula (1007, 9) which we rewrite in the form

$$\lambda_{\mathrm{H}} = \frac{\theta}{1-\theta}\frac{e^{2\theta w_{\mathrm{HH}}/kT}}{a_{\mathrm{H}}(T)}, \tag{1309, 1}$$

where $\theta$ is the fraction of sites occupied by hydrogen atoms, $a_{\mathrm{H}}(T)$ is the partition function of an absorbed H atom far removed from other H atoms, and $2w_{\mathrm{HH}}/z$ is the additive contribution to the potential energy made by each pair of absorbed H atoms which are nearest neighbours. The total interaction energy at saturation is thus $w_{\mathrm{HH}}$ per H atom. As in the previous sections we shall assume that the absorbed H atoms are effectively protons, the corresponding number of electrons having joined the main body of metallic electrons. The partition function $a_{\mathrm{H}}(T)$ then has the form

$$a_{\mathrm{H}}(T) = e^{-w_{\mathrm{H}}/kT} q_{\mathrm{H}}(T) \rho. \tag{1309, 2}$$

* Kirschfeld and Sieverts, *Zeit. Elektrochem.* **36**, 123 (1930).
† Lacher, *Proc. Camb. Phil. Soc.* **33**, 518 (1937).

Here $-w_{\mathrm{H}}$ ($>0$) is the energy required to remove an absorbed H atom, far removed from other absorbed H atoms, from its lowest state in the metal to rest at infinite dispersion; $q_{\mathrm{H}}(T)$ is the partition function for the vibrations of the absorbed H atom relative to the lattice; $\rho$ is the spin weight of the proton. Substituting (2) into (1) we have

$$\lambda_{\mathrm{H}} = \frac{\theta}{1-\theta} \frac{e^{(w_{\mathrm{H}}+2\theta w_{\mathrm{HH}})/kT}}{\rho q_{\mathrm{H}}(T)}. \tag{1309, 3}$$

We have already examined in detail in § 1008 the consequences of these formulae, and it is sufficient to recall the main features. Provided $w_{\mathrm{HH}} < 0$, there is a critical temperature $T_c$ given by

$$-w_{\mathrm{HH}}/kT_c = 2. \tag{1309, 4}$$

At temperatures below $T_c$ values of $\theta$ near $\theta = \frac{1}{2}$ are unstable, and the solid phase splits into two phases with concentrations of hydrogen symmetrically related to $\theta = \frac{1}{2}$, and with values of $\lambda_{\mathrm{H}}$ obtained from (3) by putting $\theta = \frac{1}{2}$. The curves for $\log\{\lambda(\theta)/\lambda(\frac{1}{2})\}$ against $\theta$ are antisymmetrical with respect to $\theta = \frac{1}{2}$.

If we substitute for $\lambda_{\mathrm{H}}$ from (1307, 4) into (3), we obtain for the equilibrium of hydrogen between the metal and the gas

$$\frac{\theta}{1-\theta} = \left(\frac{p}{kT}\right)^{\frac{1}{2}} e^{-(w_{\mathrm{H}}+2\theta w_{\mathrm{HH}}+\frac{1}{2}\chi_d)/kT} q_{\mathrm{H}}(T) \left\{\frac{(2\pi 2m_{\mathrm{H}} kT)^{\frac{3}{2}}}{h^3} \frac{8\pi^2 A\, kT}{2h^2}\right\}^{-\frac{1}{2}}. \tag{1309, 5}$$

The isotherms can therefore be expressed in the form

$$\frac{p(\theta)}{p(\frac{1}{2})} = \left(\frac{\theta}{1-\theta}\right)^2 e^{(2\theta-1)2w_{\mathrm{HH}}/kT}. \tag{1309, 6}$$

We have already mentioned that at temperatures below $T_c$ values of $\theta$ between $\theta'$ and $\theta''$ are unstable, and formula (6) applies only to a stable phase for values of $\theta$ outside the range $\theta'$ to $\theta''$. The pressure at which the two solid phases coexist is given by

$$p(\tfrac{1}{2}) = \frac{kT}{\{q_{\mathrm{H}}(T)\}^2} \left\{\frac{(2\pi 2m_{\mathrm{H}} kT)^{\frac{3}{2}}}{h^3} \frac{8\pi^2 A\, kT}{2h^2}\right\} e^{2(w_{\mathrm{H}}+w_{\mathrm{HH}}+\frac{1}{2}\chi_d)/kT}. \tag{1309, 7}$$

These formulae and their comparison with experiment, to be described in the following section, are due to Lacher.*

**§ 1310. Solubility of hydrogen in palladium. Comparison with experiment.** In the temperature range from 870° K. to 1470° K. and pressures up to one atmosphere the solubility of hydrogen in palladium is proportional to the square root of the pressure. Marked deviations occur at

* Lacher, *Proc. Roy. Soc.* A, **161**, 525 (1937).

lower temperatures and at higher pressures. There is a critical point at 568° K and about 20 atmospheres. The existence of two solid phases at temperatures below the critical temperature has been confirmed by X-ray investigations.* The absorption of hydrogen does not alter the lattice structure, but causes a slight expansion depending on the quantity of hydrogen absorbed. In the two-phase region two distinct lattice constants have been detected by X-rays. In the single-phase regions equilibrium sets in quickly, and one isotherm can be traced forwards and backwards without difficulty. In the two-phase region true equilibrium is only slowly attained and experimental isotherms, unless special precautions are taken, exhibit considerable hysteresis. The experimental data are shown in Figs. 2 and 3. Metastable one-phase states may be attained as shown by the data of Sieverts† in Fig. 3. True equilibrium isothermals can, however, be traced forwards and backwards without hysteresis as shown by the data of Gillespie‡ in Figs. 2 and 3.

According to the theory the isotherms for temperatures below $T_c$ have horizontal portions with mid-points at $\theta = \frac{1}{2}$. The experimental mid-points are found to correspond to $0{\cdot}29 \pm 0{\cdot}02$ hydrogen atom per palladium atom, so that saturation corresponds to $0{\cdot}58 \pm 0{\cdot}04$ hydrogen atom per palladium atom. There are good reasons§ for believing that this is the number of electrons per atom required to complete the $d$-band in palladium; this also is the number required for the similar metal nickel (§ 1110). Gold has one more valency electron per atom than palladium and, when palladium is alloyed with gold, measurements of magnetic susceptibility and electrical resistance can be simply explained, if we may suppose that the extra electron goes into the $d$-band which becomes filled when between 0·55 and 0·60 electron per atom has been added. Similarly when palladium absorbs hydrogen, its paramagnetic susceptibility decreases and becomes zero, when about 0·6 atom of hydrogen per atom of palladium has been added. This suggests that the dissolved hydrogen is ionized and that the electrons go into the $d$-band, which becomes full when about 0·6 electron per Pd atom has been supplied by H atoms. We accordingly calculate $\theta$ on the assumption that $\theta = 1$ corresponds to 0·6 H atom per Pd atom.

For comparison with experiment we combine (1309, 4) with (1309, 6), and obtain for the absorption isotherms

$$\frac{p(\theta)}{p(\frac{1}{2})} = \left(\frac{\theta}{1-\theta}\right)^2 e^{-4(2\theta-1)T_c/T} \quad (\theta < \theta' \text{ or } \theta > \theta''). \qquad (1310, 1)$$

* Linde and Borelius, *Ann. d. Phys.* **84**, 747 (1927); Krüger and Gehm, *Ann. d. Phys.* **16**, 174 (1933).

† Sieverts and Brüning, *Zeit. Physikal. Chem.* A, **163**, 409 (1932).

‡ Gillespie and Hall, *J. Am. Chem. Soc.* **48**, 1207 (1926); Gillespie and Galstaun, *J. Am. Chem. Soc.* **58**, 2565 (1936).

§ Mott and Jones, *Properties of Metals and Alloys* (Oxford, 1936), p. 192.

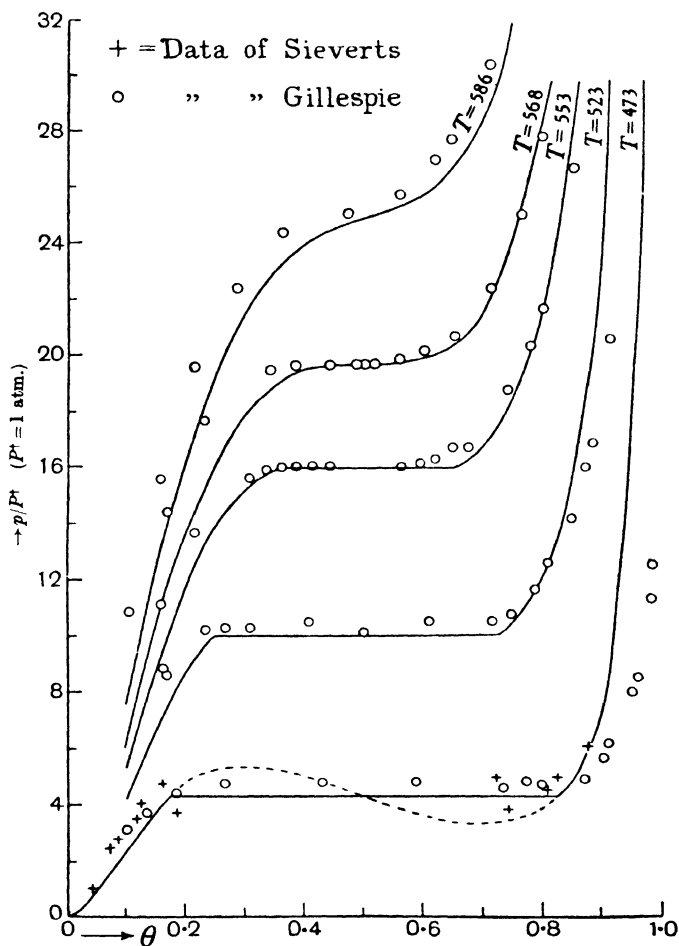



Fig. 2. Pressure-composition isotherms for hydrogen in palladium. The points are experimental, the curves calculated by Lacher. (Temperatures in ° K.)

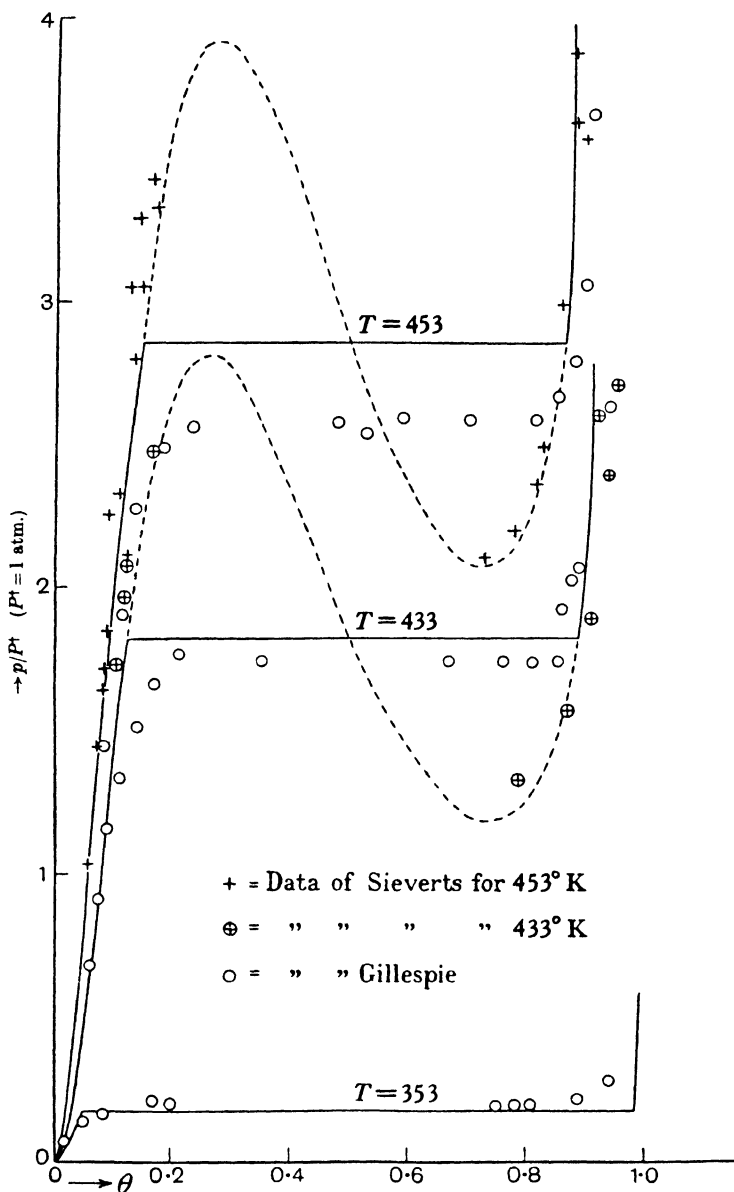



**Fig. 3.** Pressure-composition isotherms for hydrogen in palladium. The points are experimental, the curves calculated by Lacher. (Temperatures in ° K.)

This has to be supplemented by

$$p(\theta)/p(\tfrac{1}{2}) = 1 \quad (\theta' < \theta < \theta''). \tag{1310, 2}$$

At each temperature $\theta'$, $\theta''$ are determined by the intersections of (1) and (2). These two equations completely determine $p(\theta)/p(\frac{1}{2})$ as a function of $\theta$ and of $T/T_c$. The absolute value of $p(\frac{1}{2})$ at each temperature is determined by (1309, 7), which becomes on inserting numerical values

$$\frac{p(\frac{1}{2})}{P^\dagger} = 1{\cdot}2 \times 10^6 \frac{(T/500)^{\frac{7}{4}}}{\{q(T)\}^2} e^{2(w_{\mathrm{H}}+w_{\mathrm{HH}}+\frac{1}{2}\chi_d)/kT}, \tag{1310, 3}$$

where $P^\dagger$ denotes a pressure of one atmosphere. We might reasonably expect that it would be an adequate approximation to replace $q(T)$ by the partition function of a three-dimensional harmonic oscillator, but unfortunately we have no *a priori* evidence concerning an appropriate frequency to assume. In the absence of this knowledge we have to replace formula (3) by the empirical formula

$$\frac{p(\frac{1}{2})}{P^\dagger} = 4{\cdot}00 \times 10^4 . 10^{-1878/T} \tag{1310, 4}$$

due to Gillespie and Galstaun. By combining the empirical formula (4) with the theoretical formulae (1) and (2) and using the experimental value 568° K. for $T_c$, we obtain the curves in Figs. 2 and 3. The agreement between these curves and the experimental data of Gillespie is seen to be excellent.

If, instead of starting with formula (1309, 1), we use formula (1012, 6) also due to Lacher, we obtain more complicated formulae in place of (1) and (2). The agreement between theory and experiment is not appreciably affected.

§ **1311. Order-disorder in metallic alloys.** We pass on now to the consideration of the final subject of this chapter, the study of imperfections in the ordered arrangement of the atoms of a metallic alloy on the appropriate lattice points. We shall here suppose that these are the only imperfections present, so that the lattice itself is perfect, with every point occupied, and with no interlattice atoms. The imperfections then consist in the absence of or departure from the most regular possible relative arrangements of two (or more) different sorts of atoms on a given set of lattice points. Since the phenomena in question are almost entirely confined to metallic alloys, we shall speak of them in the corresponding language; the reason is that the substitutions involved in changes of orderly arrangement involve the replacements of atoms $A$ in their typical surroundings by atoms $B$ which are then in the surroundings more natural to $A$. Such interchanges are only possible with reasonable energy expenditure, if the atoms or ions $A$ and $B$ are very much alike in size or force field at short ranges. This similarity is a

characteristic of large groups of metallic atoms, and comparatively rare in other cases, so that the phenomena in question are typical of metallic alloys. It has been studied closely hitherto exclusively for binary alloys.*

It has been known for a long time† that many metallic alloys, which form for a small range of atomic ratios a single phase with a characteristic lattice structure, exhibit anomalous heat capacities and associated properties at and near a certain critical temperature. It has been shown more recently by X-ray analysis that the underlying structural change is a change, as the temperature rises, from ordered to disordered arrangement of the two sorts of atoms in the alloy. The lattice structure of the phase often undergoes no particular change near the critical point, and in other examples undergoes small changes which may alter its symmetry class, but are not of primary importance for the discussion of the change of order. Such lattice changes when they occur may usually be regarded as secondary consequences of the change of order,‡ which is the primary phenomenon. This primary change is frequently spoken of as the formation of a *superlattice*, and the change in the X-ray pattern of the lattice as the appearance of *superlattice lines*. The reason for this terminology can be simply explained.

In the state of complete disorder all lattice points concerned are occupied at random by either of the two kinds of atoms and the crystal reflects X-rays just as if all were occupied in the same average manner. The X-rays make no distinction between them. But in the ordered or partially ordered state one set of points are occupied predominantly by $A$ atoms and the other set by $B$ atoms, scattering the X-rays differently. Consequently, the X-rays distinguish between the two sets of points and new significant spacings in the crystal are shown up by the appearance of new X-ray reflections. The average crystal pattern no longer repeats so frequently when lattice points previously identical become different, so that a lattice of larger spacing (*superlattice*) is formed, and the new X-ray reflections corresponding are called *superlattice lines*. The corresponding order among the atoms is of a type which we have not hitherto discussed. Since X-rays take averages over rather large numbers of atoms the order they detect is a *long-range order*, or order relative to the set of lattice points of a whole (small) crystal. This is an entirely different property of the crystal from the degree of *local order* among the neighbours of a given atom. Atom $A$ may still be, to some degree, preferentially surrounded by $B$ atoms for nearest neighbours (the type of local order which we have already studied in §§ 814–820)

* We have space here only for a sketch of the field. For further details the reader should consult Bragg and Williams, *Proc. Roy. Soc.* A, **151**, 540 (1935), and Nix and Shockley, *Rev. Mod. Physics*, **10**, 1 (1938).

† For history, see Borelius, *Ann. d. Phys.* **20**, 57 (1934).

‡ Wilson, *Proc. Camb. Phil. Soc.* **34**, 81 (1938).

when the long-range order is absent. We shall have to consider both types of order to complete a satisfactory discussion. To start with, however, we concentrate attention on the new feature of long-range order, which we usually refer to simply as order for shortness.

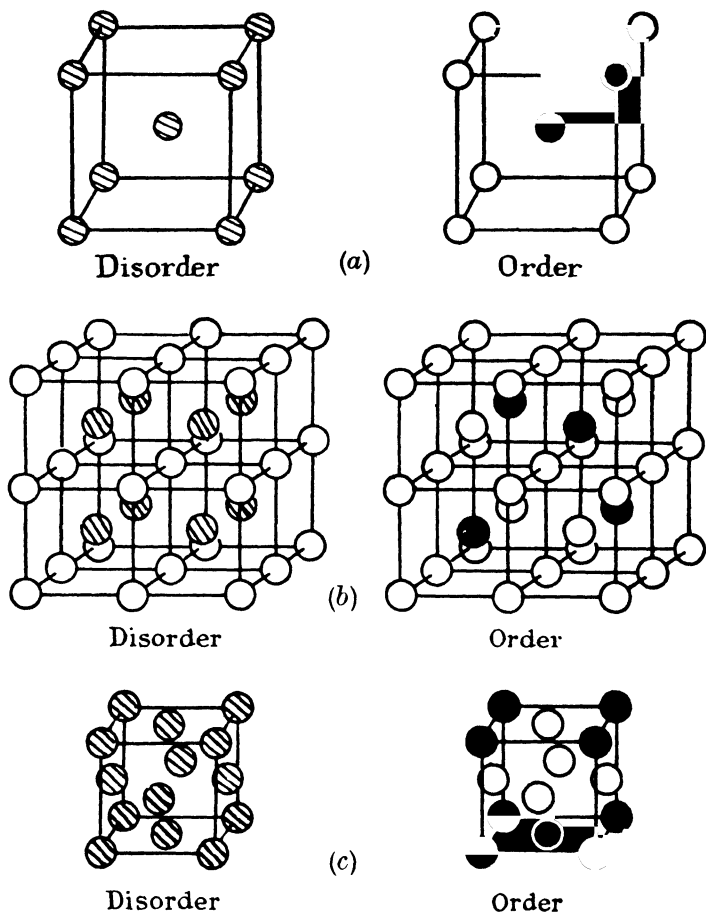



Fig. 4. Showing the arrangement of atoms in the states of complete order and complete disorder for the alloys (*a*) $\beta$-brass, CuZn, ○ Cu, ● Zn, ⊘ $\frac{1}{2}$Cu, $\frac{1}{2}$Zn; (*b*) $Fe_3Al$, ○ Fe, ● Al, ⊘ $\frac{1}{2}$Fe, $\frac{1}{2}$Al; (*c*) $Cu_3Au$, ● Au, ○ Cu, ⊘ $\frac{1}{4}$Au, $\frac{3}{4}$Cu.

Some of the types of change that have been found to occur are shown in Fig. 4. The alloy need not contain equal numbers of the two types of atoms, even for the ideal atomic ratio, and the same phenomena are exhibited in general for a definite range of atomic ratios on either side of

the ideal one. Again, not all the atoms in the alloy need take part in the changes of order. In $\beta$-brass, for example, for which the ideal atomic formula is CuZn, the lattice is body-centred cubic, all the atoms take part in the ordering, and the completely ordered and completely disordered states are shown in Fig. 4 (*a*). In the completely ordered state and at the ideal atomic ratio, all the Cu atoms occupy one simple cubic lattice, say the cube corners, and the Zn atoms the other lattice, the cube centres. In the completely disordered state every lattice point of either kind is occupied indifferently by either atom. In the alloy $Fe_3Al$ on the other hand only half the atoms take part in the changes of order. The lattice is again body-centred cubic, and two-thirds of the Fe atoms occupy permanently one simple cubic lattice at all temperatures. The remaining atoms, equal numbers of Fe and Al, occupy the remaining lattice points at the cube centres—in the ordered state forming a rock salt lattice (two interpenetrating face-centred cubic lattices one of Fe and the other of Al), and in the disordered occupying all points of the simple cubic lattice indifferently. In the alloy $Cu_3Au$ again all the atoms take part in the changes of order. In the ordered state the Au atoms occupy one of the four simple cubic lattices into which a face-centred cubic lattice can be dissected, and the Cu atoms occupy the other three. In the disordered state all points of the face-centred lattice are occupied indifferently by Cu and Au in the ratio 3 : 1.

In order to study the equilibrium degree of order theoretically it is only necessary to construct the configurational partition function factor $\Gamma(T)$ for the alloy. We shall neglect in this study, which cannot attempt to be exhaustive, any effect of the degree of order on the normal modes of the lattice or on the lattice constants or lattice symmetry.

**§ 1312. Definition of the degree of (long-range) order in an alloy with two equivalent sub-lattices.** Let us suppose that in a given specimen of an alloy there are $N^l$ lattice points occupied by $N^l$ atoms of two kinds, all of which take part in the ordering. Other atoms, if present, of the same or different kinds, on other lattice points which take no part in the ordering may be ignored. It is convenient to emphasize that we are concerned with a given number of lattice points rather than atoms by continuing to use the notation $N^l$, since the atoms are of two kinds and may be present in varying proportions.

The essential new feature of long-range order is, as explained in § 1311, that the $N^l$ lattice points can be divided into classes (sub-lattices). We begin by considering in detail the case where there are only two sub-lattices symmetrically related to each other and postpone to §§ 1324, 1325 a shorter review of a more complicated case. We therefore assume that there are $N^l$

lattice points (sites), $\frac{1}{2}N^l$ of type $a$ and $\frac{1}{2}N^l$ of type $b$; each site $a$ has $z$ sites $b$ as its nearest neighbours, and each site $b$ has $z$ sites $a$ as its nearest neighbours.

For simplicity let us begin by discussing the special case when there are equal numbers $\frac{1}{2}N^l$ of each kind of atom $A$ and $B$. We can without loss of generality assume that at least half of the $A$ atoms are on $a$ sites. If then we denote the number of $A$ atoms on $a$ sites by $\frac{1}{2}(1+s)\,\frac{1}{2}N^l$, the parameter $s$ satisfies the inequality $0 \leqslant s \leqslant 1$. Since all $A$ atoms not on $a$ sites are on $b$ sites, and all sites not occupied by $A$ atoms are occupied by $B$ atoms, we have the distribution given in Table 2.

TABLE 2

*Distribution of A and B atoms (equal numbers) on a and b sites*

| | |
|---|---|
| $A$ atoms on $a$ sites. $\frac{1}{2}(1+s)\,\frac{1}{2}N^l$; | $A$ atoms on $b$ sites: $\frac{1}{2}(1-s)\,\frac{1}{2}N^l$; |
| $B$ atoms on $a$ sites: $\frac{1}{2}(1-s)\,\frac{1}{2}N^l$; | $B$ atoms on $b$ sites: $\frac{1}{2}(1+s)\,\frac{1}{2}N^l$. |

When $s = 1$, all the $A$ atoms are on $a$ sites and all the $B$ atoms are on $b$ sites; this is the state of perfect order. When $s = 0$, there are as many $A$'s on $a$ sites as on $b$ sites, and also as many $B$'s on $a$ sites as on $b$ sites; this is the state of complete disorder and the distinction between $a$ sites and $b$ sites has disappeared. Intermediate values of $s$ correspond to intermediate degrees of order, and $s$ is therefore a measure of, and may be called, *the degree of order*.

The case of unequal numbers of $A$ atoms and $B$ atoms is only slightly more complicated. Let the number of $A$ atoms be $x_A N^l$; without loss of generality we may suppose $x_A \leqslant \frac{1}{2}$. Let the number of $B$ atoms be $x_B N^l$, so that

$$x_A + x_B = 1. \tag{1312, 1}$$

If the number of $A$ atoms on $a$ sites is $x_A\,\frac{1}{2}(1+s)\,N^l$, the distribution of the two kinds of atoms on the two kinds of sites must be as given in Table 3.

TABLE 3

*Distribution of A and B atoms (unequal numbers) on a and b sites*

| | |
|---|---|
| $A$ atoms on $a$ sites: $\frac{1}{2}x_A(1+s)\,N^l$; | $A$ atoms on $b$ sites: $\frac{1}{2}x_A(1-s)\,N^l$; |
| $B$ atoms on $a$ sites: $\frac{1}{2}(x_B - x_A s)\,N^l$; | $B$ atoms on $b$ sites: $\frac{1}{2}(x_B + x_A s)\,N^l$. |

It is again clear that $s = 1$ corresponds to the highest possible order and $s = 0$ to complete disorder. We may therefore again call *$s$ the degree of order*.

**§ 1313. Determination of equilibrium properties.** As usual all the equilibrium properties are determined by the partition function. We assume that we need consider only the configurational factor of the partition function, and as previously we denote this by $\Gamma(T)$. This is equivalent to assuming

that the normal modes of the lattice are independent of the configurations. Every single distinguishable configuration of the alloy will contribute one term to $\Gamma(T)$, but to make progress we group these states according to the degree of order $s$. We therefore write formally

$$\Gamma(T) = \Sigma_s \Gamma(T, s), \qquad (1313, 1)$$

where $\Gamma(T, s)$ denotes the sum of all terms of given $s$. Exactly as in many other cases which we have already met, it can be shown that we may replace $\log \Gamma(T)$ by $\log \Gamma(T, s^*)$, where $s^*$ is the value of $s$ for which $\Gamma(T, s)$ has the greatest value. When we use this procedure the problem of determining the equilibrium properties has two stages: (1) to evaluate $\Gamma(T, s)$ for arbitrary $s$, and (2) to find the value $s^*$ of $s$ which maximizes $\Gamma(T, s)$. Translated into thermodynamic nomenclature, these two stages are: (1) to evaluate the free energy $F(T, s)$ for arbitrary $s$, and (2) to find the value $s^*$ of $s$ which minimizes the free energy $F(T, s)$. When no confusion can arise we often drop the asterisk, and use $s$ to denote the equilibrium value.

We now consider the problem of evaluating $\Gamma(T, s)$. By definition of $\Gamma(T, s)$ we have

$$\Gamma(T, s) = \Sigma_\tau e^{-W_\tau/kT}, \qquad (1313, 2)$$

where $W_\tau$ denotes the configurational energy of the state $\tau$ and the summation extends over all states $\tau$ of given order $s$. The number of such states is equal to the number of ways of dividing the $\frac{1}{2}N^l$ sites $a$ into two groups and the $\frac{1}{2}N^l$ sites $b$ into two groups, the numbers of sites in each group being given in Table 3. If we denote this number by $g(s)$, we have then

$$g(s) = \frac{[\frac{1}{2}N^l]!}{[x_A(1+s)\,\frac{1}{2}N^l]!\,[(x_B - x_A s)\,\frac{1}{2}N^l]!}\,\frac{[\frac{1}{2}N^l]!}{[x_A(1-s)\,\frac{1}{2}N^l]!\,[(x_B + x_A s)\,\frac{1}{2}N^l]!}. \qquad (1313, 3)$$

Using Stirling's theorem we can rewrite this as

$$\log g(s) = -\tfrac{1}{2}N^l\{(x_A + x_A s)\log(x_A + x_A s) + (x_B - x_A s)\log(x_B - x_A s) + (x_A - x_A s)\log(x_A - x_A s) + (x_B + x_A s)\log(x_B + x_A s)\}. \qquad (1313, 4)$$

We may note in passing that in the absence of long-range order $s = 0$, and formula (3) reduces to

$$g(0) = \left\{\frac{[\frac{1}{2}N^l]!}{[x_A\,\frac{1}{2}N^l]!\,[x_B\,\frac{1}{2}N^l]!}\right\}^2; \qquad (1313, 5)$$

for large $N^l$ this is effectively equivalent to

$$g(0) \simeq \frac{N^l!}{[x_A N^l]!\,[x_B N^l]!} = \Sigma_s g(s). \qquad (1313, 6)$$

Using a notation resembling that used in the treatment of regular assemblies in § 610, we now define $\overline{\overline{W}}(s)$ by the relation

$$\Sigma_\tau e^{-W_\tau/kT} = g(s)\, e^{-\overline{\overline{W}}(s)/kT}. \qquad (1313, 7)$$

The equilibrium configurational energy for given $s$ is $\overline{W}(s)$ given by

$$\Sigma_\tau W_\tau e^{-W_\tau/kT} = \overline{W}(s)\,\Sigma_\tau e^{-W_\tau/kT}. \qquad (1313, 8)$$

It follows at once from equation (7) that the configurational free energy $F(s)$ for given $s$ is

$$F(s) = -kT\log g(s) + \overline{\overline{W}}(s), \qquad (1313, 9)$$

while the configurational energy $E(s)$ is

$$E(s) = \overline{W}(s). \qquad (1313, 10)$$

From (7) and (8) we can verify the necessary equality

$$\overline{W}(s) = \frac{\partial[\overline{\overline{W}}(s)/T]}{\partial[1/T]}. \qquad (1313, 11)$$

Since by formula (4) we know $g(s)$, the usefulness of formula (9) depends on our being able to evaluate $\overline{\overline{W}}(s)$ as a function of $s$. The exact evaluation of $\overline{\overline{W}}(s)$ is prohibitively laborious, and we postpone its discussion to § 1316. There are, however, several methods of obtaining useful approximate formulae for $\overline{\overline{W}}(s)$, of various degrees of accuracy. We shall describe several of these methods. Before considering them we must specify more closely the source of the energy differences between the various configurations.

The main contribution to the $W_\tau$ may be expected to come from the interaction energy of pairs of nearest neighbours. The interaction energy of $AA$, $BB$, and $AB$ pairs is different, and the numbers of such pairs varies over the set of configurations of given $s$. Naturally this cannot be expected to be rigorously the whole contribution; more distant pairs may contribute. Nor is it certain that the configurational energy can be rigorously expressed as the sum of contributions by interacting pairs. The interaction of a pair may be modified by the nature of its surroundings. Further, there may quite possibly be a term in $W_\tau$ which depends directly on the long-range order $s$, and is independent of the details of the configuration for given $s$. Such a term could arise from the effect on the energies of the conduction electrons due to the changing perfection of the superlattice. We have, however, no means of estimating any of these effects which are probably fairly small. We must be content with the customary approximation of taking the total interaction energy as the sum of characteristic terms contributed by each pair of nearest neighbours. In any specified configuration $\tau$ the configurational energy $W_\tau$ is therefore taken to be given by

$$W_\tau = -\frac{2}{z}\{n_{AA}\chi_{AA} + n_{AB}\chi_{AB} + n_{BB}\chi_{BB}\}, \qquad (1313, 12)$$

where $-2\chi_{AA}/z, \ldots$ are the energies of interaction of an $AA, \ldots$ pair of nearest neighbours and $n_{AA}, \ldots$ are the numbers of such pairs. We have defined the $\chi$'s as in Chapter VIII so that the energy of a piece of pure $A$ (or $B$) containing $N_A$ (or $N_B$) atoms is $-N_A\chi_{AA}$ (or $-N_B\chi_{BB}$).

**§ 1314. Zeroth approximation (Bragg and Williams).** The simplest method of approximation, used by Bragg and Williams,* is the exact analogue of the crude treatment of regular solutions described in § 818. This approximation consists in replacing the true value of $W_r$ for each configuration of given $s$ by the simple (unweighted) average $W_{Av}(s)$ for all states of given $s$. Since for given $s$ this $W_{Av}(s)$ is independent of the temperature, we have according to this approximation

$$\overline{\overline{W}}(s) = \overline{W}(s) = W_{Av}(s). \qquad (1314, 1)$$

This approximation is equivalent to assuming purely random arrangements of the $A$ and $B$ atoms on each site of a chosen pair of neighbours, so long as the given value of $s$ is preserved. We have then

$$W_{Av}(s) = -\frac{2}{z}\{(n_{AA})_{Av}\chi_{AA} + (n_{AB})_{Av}\chi_{AB} + (n_{BB})_{Av}\chi_{BB}\}, \qquad (1314, 2)$$

where $(n_{AA})_{Av}, \ldots$ are the unweighted averages of $n_{AA}, \ldots$ for all configurations of the given $s$.

From Table 3 we note that the average number of $A$ atoms on $a$ sites is $x_A(1+s)\frac{1}{2}N^l$; each of these has $z$ nearest neighbour $b$ sites, and the average fraction of these occupied by $A$ atoms is $x_A(1-s)$. Therefore

$$(n_{AA})_{Av} = \tfrac{1}{2}N^l z x_A^2(1-s^2). \qquad (1314, 3)$$

Similarly

$$(n_{AB})_{Av} = \tfrac{1}{2}N^l z(2x_A x_B + 2x_A^2 s^2), \qquad (1314, 4)$$

$$(n_{BB})_{Av} = \tfrac{1}{2}N^l z(x_B^2 - x_A^2 s^2). \qquad (1314, 5)$$

On inserting these values into (2), we find

$$W_{Av}(s) = -N^l\{x_A^2\chi_{AA} + 2x_A x_B\chi_{AB} + x_B^2\chi_{BB}\} + N^l x_A^2 s^2\{\chi_{AA} - 2\chi_{AB} + \chi_{BB}\}. \qquad (1314, 6)$$

It is customary to define an energy $w$ by

$$2\chi_{AB} - \chi_{AA} - \chi_{BB} = w; \qquad (1314, 7)$$

substituting this into (6), we have

$$\begin{aligned} W_{Av}(s) &= -N^l\{x_A^2\chi_{AA} + 2x_A x_B\chi_{AB} + x_B^2\chi_{BB}\} - N^l x_A^2 s^2 w \\ &= W(0) - N^l x_A^2 s^2 w, \end{aligned} \qquad (1314, 8)$$

where $W(0)$ is the value of $W$ for the state of complete disorder. We would warn the reader that $w$ is defined with the opposite sign to that of $w_{AB}$ in § 814; thus $w$ is an *energy of unmixing*.

Using $W_{Av}(s)$ given by (8) for $\overline{W}(s)$ and the value of $g(s)$ given by (1313, 4),

* Bragg and Williams, *Proc. Roy. Soc.* A, **145**, 699 (1934).

we obtain for the configurational free energy according to (1313, 9)

$$F(s) = \tfrac{1}{2}N^l kT\{(x_A + x_A s)\log(x_A + x_A s) + (x_B - x_A s)\log(x_B - x_A s) + (x_A - x_A s)\log(x_A - x_A s) + (x_B + x_A s)\log(x_B + x_A s)\} + W(0) - N^l x_A^2 s^2 w. \qquad (1314, 9)$$

In the simplest case of equal numbers of $A$ and $B$ atoms, we have $x_A = x_B = \frac{1}{2}$, and formula (9) reduces to

$$F(s) = \tfrac{1}{2}N^l kT\{(1+s)\log(1+s) + (1-s)\log(1-s) - 2\log 2\} + W(0) - \tfrac{1}{2}N^l \tfrac{1}{2}s^2 w; \qquad (1314, 10)$$

alternatively,

$$F(s) - F(1) = \tfrac{1}{2}N^l kT\{(1+s)\log(1+s) + (1-s)\log(1-s) - 2\log 2\} + \tfrac{1}{2}N^l \tfrac{1}{2}(1-s^2)\,w. \qquad (1314, 11)$$

The formula for the configurational energy corresponding to formula (9) for the free energy is

$$E(s) = E(0) - N^l x_A^2 s^2 w = E(1) + N^l x_A^2 (1-s^2)\,w. \qquad (1314, 12)$$

For the simple case $x_A = x_B = \frac{1}{2}$ this becomes

$$E(s) = E(0) - N^l \tfrac{1}{4}s^2 w = E(1) + N^l \tfrac{1}{4}(1-s^2)\,w. \qquad (1314, 13)$$

We can eliminate $w$ between these two equations and obtain

$$\frac{E(s) - E(1)}{E(0) - E(1)} = 1 - s^2. \qquad (1314, 14)$$

The quantity $1 - s^2$, which occurs passim, is equivalent to the degree of disorder introduced by Borelius.*

**§ 1315. Equilibrium value of $s$ by zeroth approximation (Gorsky, Bragg and Williams).** Having obtained an approximate formula for $F(s)$ we have, to this approximation, completed the first stage in the determination of the equilibrium properties. The second stage is most conveniently dealt with as a problem in pure thermodynamics. We have a formula for the free energy $F(s)$ for an arbitrary value of $s$; the equilibrium state of the assembly is obtained by minimizing $F(s)$. According to (1314, 9) the condition $\partial F/\partial s = 0$ gives

$$\log\frac{(x_A + x_A s)(x_B + x_A s)}{(x_A - x_A s)(x_B - x_A s)} = \frac{4x_A w}{kT}s. \qquad (1315, 1)$$

This can be transformed to the equivalent form

$$\frac{s/x_B}{1 + x_A s^2/x_B} = \tanh\left(\frac{2x_A w}{kT}s\right). \qquad (1315, 2)$$

* Borelius, *Ann. d. Phys.* **20**, 57 (1934).

In the simplest case $x_A = x_B = \frac{1}{2}$, this reduces to

$$\frac{2s}{1+s^2} = \tanh\left(\frac{w}{kT}s\right), \qquad (1315, 3)$$

which is equivalent to

$$s = \tanh\left(\frac{w}{2kT}s\right). \qquad (1315, 4)$$

For all values of $w/kT$ one root of (2) is zero. When $w<0$ this is the only root and it corresponds to a minimum of $F(s)$. There is then no long-distance order and the alloy reduces to a regular solution of the type discussed in

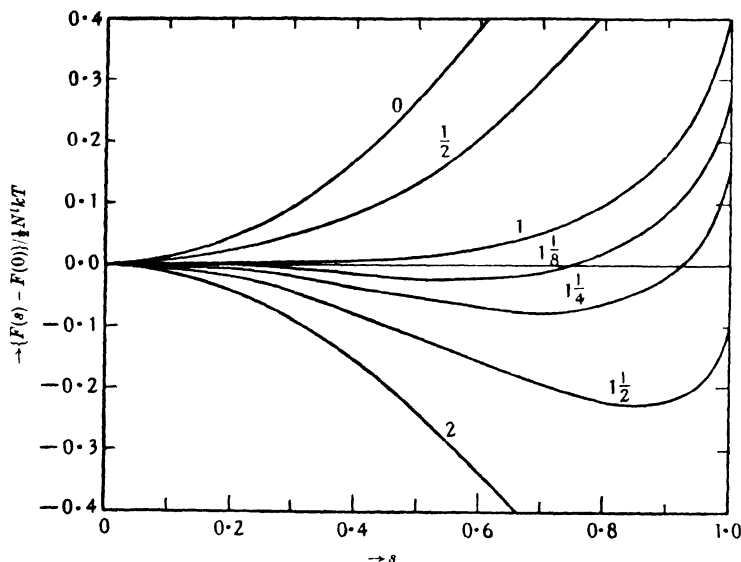



Fig 5. Dependence of the configurational free energy $F(s)$ on the degree of order $s$ for alloy of composition $AB$ according to the zeroth (B.-W.) approximation for various temperatures. The numbers attached to the curves are values of $\frac{1}{2}w/kT$ or $T_c/T$.

Chapter VIII. The formulae there deduced for liquid mixtures apply as well, if not better, to solid solutions. When $w>0$ at high temperatures (small values of $w/kT$) the root $s=0$ is the only root and it corresponds to a minimum of $F(s)$. There is again no long-distance order and the alloy behaves as a regular solution. At low enough temperatures (large values of $w/kT$) there is another root $0 \leqslant s \leqslant 1$, and this root corresponds to a minimum of $F(s)$ while the root $s=0$ now corresponds to a maximum. This is made clear in Fig. 5, where $F(s)$ is plotted against $s$ for various values of $w/kT$, with $x_A = x_B = \frac{1}{2}$. Thus there exists a temperature $T_c$ such that at temperatures below $T_c$ the equilibrium value of $s$ is greater than 0 and decreases

as the temperature increases; the equilibrium value of $s$ becomes zero at the temperature $T_c$ and remains zero at all higher temperatures. By analogy with the ferromagnetic Curie point, discussed in Chapter XIV, one may call this temperature the *Curie point* or *Curie temperature for order-disorder.* At the Curie temperature $T_c$ there are two coincident roots at $s = 0$.

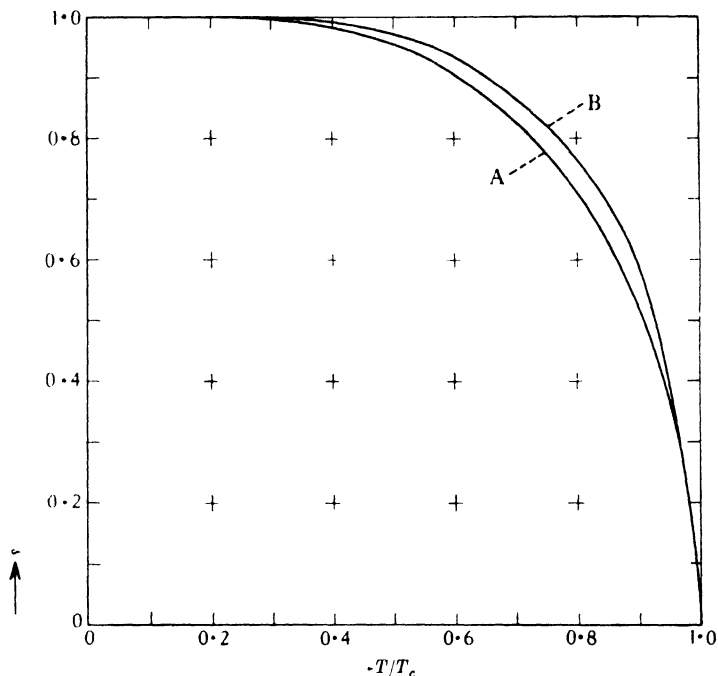



Fig 6 Equilibrium degree of order as function of temperatures for alloy of composition $AB$. A Zeroth approximation (Gorsky, Bragg and Williams). B First approximation (Bethe) for $z = 8$

Consequently $T_c$ is determined by the conditions

$$s = 0, \quad \partial F/\partial s = 0, \quad \partial^2 F/\partial s^2 = 0. \qquad (1315, 5)$$

Using formula (1314, 9) for $F(s)$, these conditions lead to

$$kT_c = 2x_A x_B w. \qquad (1315, 6)$$

Since by definition $x_A + x_B = 1$, the maximum value of $x_A x_B$ occurs when $x_A = x_B = \frac{1}{2}$. Hence the critical temperature has a maximum value given by

$$kT_c = \tfrac{1}{2}w \quad (x_A = x_B = \tfrac{1}{2}). \qquad (1315, 7)$$

In virtue of (7) we can rewrite (4) as

$$\frac{s}{\operatorname{arc\,tanh} s} = \frac{T}{T_c}. \tag{1315, 8}$$

This relation between $s$ and $T$ is shown in Fig. 6. At temperatures below $T_c$ the configurational energy $E(s)$ is obtained by substituting into (1314, 14) the value of $s$ determined by (8). We thus obtain curve A in Fig. 7. From the slope of this curve we see that the configurational contribution to the heat capacity increases with $T$ to a maximum value at $T_c$ and then according to the present approximation falls to zero. A more exact discussion of the configurational heat capacity is given in § 1319.

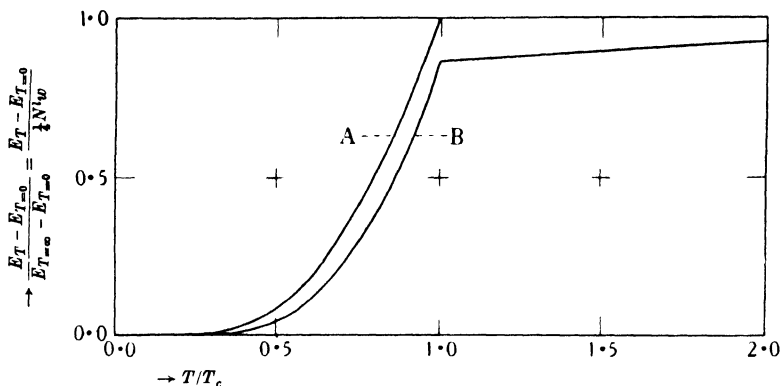



Fig. 7. Equilibrium configurational energy for alloy of composition $AB$ as function of temperature. A: Zeroth approximation (Bragg and Williams). B: First approximation (Bethe) for $z = 8$.

Most of the formulae of this section are due to Bragg and Williams,* but the simple case $x_A = x_B = \frac{1}{2}$ has previously been discussed by Gorsky,† who obtained equations (4) and (7) and Fig. 6.

**§ 1316. The evaluation of $F(s)$ as a power series in $w/kT$ (Kirkwood).** It was pointed out by Kirkwood‡ that it is in principle possible to evaluate $\overline{\overline{W}}(s)$ to any desired degree of accuracy. We can rewrite equation (1313, 7), which defines $\overline{\overline{W}}(s)$, in the form

$$\overline{\overline{W}}(s)/kT = \log g(s) - \log \Sigma_r\, e^{-W_r/kT}. \tag{1316, 1}$$

* Bragg and Williams, *Proc. Roy. Soc.* A, **145**, 699 (1934); **151**, 540 (1935).

† Gorsky, *Zeit. Phys.* **50**, 64 (1928). The quantity $\alpha$ called degree of order by Gorsky is equal to $\frac{1}{2}(1+s)$ where $s$ is the quantity which Bragg and Williams call degree of order. The statement by Bragg and Williams (p. 542) that Gorsky's formula is incorrect appears to be mistaken. Gorsky's formula (11) is in fact equivalent to formula (4) of this section.

‡ Kirkwood, *J. Chem. Phys.* **6**, 70 (1938).

On expanding the exponentials this can be reduced to the form

$$\frac{\overline{\overline{W}}(s)}{kT} = -\log\left[1-\frac{W_{Av}}{kT}+\frac{(W^2)_{Av}}{2!(kT)^2}-\frac{(W^3)_{Av}}{3!(kT)^3}+\dots\right], \qquad (1316,2)$$

where $(W^r)_{Av}$ denotes the unweighted average of $W^r$ over all states $\tau$ of given $s$. Thus provided we can calculate the unweighted average of $W^r$ over all states of given $s$ we can derive $\overline{\overline{W}}(s)$ exactly. On further expanding the logarithm in (2) we find

$$\overline{\overline{W}}(s) = W_{Av}-\frac{1}{2!kT}\{(W^2)_{Av}-(W_{Av})^2\}$$
$$+\frac{1}{3!(kT)^2}\{(W^3)_{Av}-3W_{Av}(W^2)_{Av}+2(W_{Av})^3\}+\dots. \qquad (1316,3)$$

Kirkwood has evaluated $(W^2)_{Av}$, $(W^3)_{Av}$ for the case $x_A = x_B = \frac{1}{2}$, and thus has shown that*

$$\overline{\overline{W}}(s)-W(1) = \tfrac{1}{2}N^lw\left\{\tfrac{1}{2}(1-s^2)-\frac{w}{zkT}\tfrac{1}{8}(1-s^2)^2-\left(\frac{w}{zkT}\right)^2\tfrac{1}{12}s^2(1-s^2)^2+\dots\right\}, \qquad (1316,4)$$

where $w$ is defined by (1314, 7). Using (4) and (1313, 4) with $x_A = x_B = \frac{1}{2}$, in (1313, 9) we obtain

$$F(s)-F(1) = \tfrac{1}{2}N^lkT\{(1+s)\log(1+s)+(1-s)\log(1-s)-2\log 2\}$$
$$+\tfrac{1}{2}N^lw\left\{\tfrac{1}{2}(1-s^2)-\frac{w}{zkT}\tfrac{1}{8}(1-s^2)^2-\left(\frac{w}{zkT}\right)^2\tfrac{1}{12}s^2(1-s^2)^2+\dots\right\}. \qquad (1316,5)$$

The zeroth approximation corresponds to retaining only the first term in (4) and ignoring the terms in $(W/zkT)$, $(W/zkT)^2$, .... This is most easily verified by comparing formula (5) with (1314, 11). Formally we can obtain the formulae of the zeroth approximation by letting $z\to\infty$.

The equilibrium value of $s$ is obtained by minimizing (5). We thus obtain instead of (1315, 1)

$$\log\frac{1+s}{1-s} = \frac{w}{kT}s\left\{1-\frac{w}{zkT}\tfrac{1}{2}(1-s^2)+\left(\frac{w}{zkT}\right)^2\tfrac{1}{6}(1-s^2)(1-3s^2)+\dots\right\}. \qquad (1316,6)$$

This equation, like (1315, 1), always has one solution $s = 0$. At sufficiently low temperatures there is also a non-zero root if $w > 0$. It can be verified that when there is a non-zero root it corresponds to a minimum in $F(s)$ and the zero root corresponds to a maximum. When the zero root is the only one, it corresponds to a minimum. The Curie temperature $T_c$ at which the two roots merge into each other is given by the conditions

$$s = 0, \quad \partial F/\partial s = 0, \quad \partial^2F/\partial s^2 = 0, \qquad (1316,7)$$

* The sign of the last term is given wrong by Kirkwood. See Chang, *Proc. Camb. Phil. Soc.* **35**, 277 (1939).

which lead to
$$2\frac{kT_c}{w} = 1 - \frac{1}{2}\frac{w}{zkT_c} + \frac{1}{6}\left(\frac{w}{zkT_c}\right)^2 + \dots, \qquad (1316, 8)$$

as compared with the zeroth approximation (1315, 7). For comparison with a formula to be obtained later, it is convenient to rewrite (8) in the form

$$1 - \frac{2}{z} = 1 - \frac{w}{zkT_c} + \frac{1}{2}\left(\frac{w}{zkT_c}\right)^2 - \frac{1}{6}\left(\frac{w}{zkT_c}\right)^3 + \dots. \qquad (1316, 9)$$

These formulae due to Kirkwood should be exact if one includes a sufficient number of terms. Unfortunately the series in (4) converges rather slowly at temperatures below $T_c$, and it would probably require immense labour to compute the coefficients of the higher terms.

§ **1317. Quasi-chemical treatment.** We shall now describe an approximation which is the exact analogue of the treatment of regular solutions given in § 819. It is convenient for the sake of brevity to use a different notation from that of the previous sections, and to transcribe the notation at a later stage. We continue to denote the number of sites of each kind by $\frac{1}{2}N^l$, but we denote the number of $A$ atoms on $a$ sites by $R$ and the number of $A$ atoms on $b$ sites by $Q$. The distribution of the two kinds of atoms over the two kinds of sites is then that given in Table 4.

TABLE 4

*Distribution of A and B atoms on a and b sites*

| | |
|---|---|
| $A$ atoms on $a$ sites: $R$; | $B$ atoms on $a$ sites: $\frac{1}{2}N^l - R$; |
| $A$ atoms on $b$ sites: $Q$; | $B$ atoms on $b$ sites: $\frac{1}{2}N^l - Q$. |

We now construct a table for the number of pairs of neighbouring sites occupied in the four possible ways. We denote by $zX$ the number of pairs with an $A$ atom on both sites of the pair. This determines the numbers of pairs occupied in the three other ways as given in Table 5.

TABLE 5

*Distribution of A and B atoms on pairs of neighbouring sites (one a site and one b site)*

| | |
|---|---|
| $A$ on $a$, $B$ on $b$: $z(R-X)$; | $B$ on $a$, $A$ on $b$: $z(Q-X)$; |
| $A$ on $a$, $A$ on $b$: $zX$; | $B$ on $a$, $B$ on $b$: $z(\frac{1}{2}N^l - R - Q + X)$. |

The total number of pairs is $\frac{1}{2}N^l z$. We denote by $g(R, Q, X)$ the number of distinguishable configurations with specified values of $R$, $Q$, $X$, and by $W(R, Q, X)$ the energy of each of these configurations. Specifying the values of $R$ and $Q$ is equivalent to specifying the composition $x$ of the alloy and the degree of order $s$ as in the previous treatment. The present treatment goes a stage further in grouping together states of the same $X$, as well as the

same $R$, $Q$. As a result of this new method of grouping we can immediately write down an exact formula for the energy $W(R, Q, X)$, namely

$$\begin{aligned} W(R,Q,X) &= -2X\chi_{AA} - 2(R+Q-2X)\chi_{AB} - 2(\tfrac{1}{2}N^l - R - Q + X)\chi_{BB} \\ &= -2(R+Q)\chi_{AB} - 2(\tfrac{1}{2}N^l - R - Q)\chi_{BB} + 2Xw, \qquad (1317,1) \end{aligned}$$

where as before $$w = 2\chi_{AB} - \chi_{AA} - \chi_{BB}. \qquad (1317,2)$$

On the other hand we have no exact simple formula for $g(R, Q, X)$. The fundamental approximation of the present method is that for given $R$, $Q$ and varying $X$ we take $g(R, Q, X)$ as proportional to the total number of ways one can divide $\frac{1}{2}zN^l$ entities into four groups containing the number of entities given in Table 5. To be precise we assume as an approximation

$$g(R,Q,X) = h(R,Q)\frac{[\frac{1}{2}zN^l]!}{[z(R-X)]!\,[zX]!\,[z(Q-X)]!\,[z(\frac{1}{2}N^l - R - Q + X)]!}. \qquad (1317,3)$$

We would emphasize that this formula for $g(R, Q, X)$ cannot be accurate, because we cannot treat the pairs of neighbours as independent entities. Obviously as soon as we fix the nature of the occupation of a certain pair of sites, this limits the possible manners of occupation of other pairs which share a site with the first pair. *A priori* it is difficult to see how bad is the approximation involved in (3). At the present stage it is just a guess. We shall find, however, that, without any further assumptions, formula (3) leads to results which strongly suggest that it is in fact a strikingly useful approximation.

For our present purpose we do not require to know the factor $h(R, Q)$ in $g(R, Q, X)$ which is independent of $X$. It is, however, not difficult to determine this factor by considering the value, say $X_0$, of $X$ which maximizes $g(R, Q, X)$. As usual it can be shown that this maximum value $g(R, Q, X_0)$ differs from the sum of $g(R, Q, X)$ over all $X$ only by a factor which is trivial for large assemblies. But the sum of $g(R, Q, X)$ over all $X$ is simply $g(R, Q)$, the total number of ways of distributing $R$ atoms $A$ on the $a$ sites and $Q$ atoms $A$ on the $b$ sites. We have therefore

$$g(R,Q,X_0) \simeq \Sigma_X\, g(R,Q,X) = g(R,Q) = \frac{[\frac{1}{2}N^l]!}{R![\frac{1}{2}N^l - R]!}\,\frac{[\frac{1}{2}N^l]!}{Q![\frac{1}{2}N^l - Q]!}. \qquad (1317,4)$$

Combining (4) with (3) and the analogous formula with $X_0$ in the place of $X$, we can eliminate $h(R, Q)$ and find

$$\begin{aligned} g(R,Q,X) &= \frac{[\frac{1}{2}N^l]!}{R![\frac{1}{2}N^l - R]!}\,\frac{[\frac{1}{2}N^l]!}{Q![\frac{1}{2}N^l - Q]!} \\ &\times \frac{[z(R-X_0)]!\,[zX_0]!\,[z(Q-X_0)]!\,[z(\frac{1}{2}N^l - R - Q + X_0)]!}{[z(R-X)]!\,[zX]!\,[z(Q-X)]!\,[z(\frac{1}{2}N^l - R - Q + X)]!}. \qquad (1317,5) \end{aligned}$$

Now the value of $X_0$ which maximizes $g(R, Q, X)$ is undoubtedly the value which corresponds to complete randomness and is given by

$$X_0 = RQ/\tfrac{1}{2}N^l. \qquad (1317, 6)$$

We have merely to substitute this value of $X_0$ into (5) to obtain a formula for $g(R, Q, X)$ as an explicit function of $N^l$, $R$, $Q$, $X$. For the sake of brevity we shall, however, retain $X_0$, which we may now regard as an abbreviation for $RQ/\frac{1}{2}N^l$. At the present stage formula (5) is merely a guess, in fact a guess equivalent to (3). However, a formula precisely equivalent to (5) has been obtained by Chang,* using an entirely different procedure which we shall describe briefly in § 1323. We provisionally assume the approximate validity of either (3) or (5), and are able to complete the treatment without any further assumptions.

The complete configurational partition function can be written as

$$\Gamma(T) = \Sigma_R \Sigma_X g(R, Q, X)\, e^{-W(R,Q,X)/kT}, \qquad (1317, 7)$$

the inner summation extending over all $X$ for given $R$, $Q$ and the outer summation over all $R$, $Q$, keeping $R+Q$ constant. As usual we may replace each sum by its maximum term. Let us first take $R$, $Q$ as fixed and maximize with respect to $X$. $\Gamma(T)$ then reduces to

$$\Gamma(T) = \Sigma_R g(R, Q, X)\, e^{-W(R,Q,X)/kT}. \qquad (1317, 8)$$

with $X$ determined by

$$\frac{\partial}{\partial X}\{\log g(R, Q, X) - W(R, Q, X)/kT\} = 0. \qquad (1317, 9)$$

Substituting the accurate formula (1) for $W(R, Q, X)$ and the tentative formula (3) for $g(R, Q, X)$, and using Stirling's theorem, we find

$$\log(R-X) - \log X + \log(Q-X) - \log(\tfrac{1}{2}N^l - R - Q + X) - 2w/zkT = 0. \qquad (1317, 10)$$

This can be rewritten as

$$(R-X)(Q-X) = X(\tfrac{1}{2}N^l - R - Q + X)\, e^{2w/zkT}, \qquad (1317, 11)$$

or as

$$\frac{[A \text{ on } a;\ B \text{ on } b]\ [B \text{ on } a;\ A \text{ on } b]}{[A \text{ on } a;\ A \text{ on } B]\ [B \text{ on } a;\ B \text{ on } b]} = e^{2w/zkT}, \qquad (1317, 12)$$

where each [ ] denotes the number of pairs of neighbouring sites occupied in the manner indicated inside the brackets. Formula (11) is the exact analogue of formulae (610, 9) and (819, 1) used for regular assemblies in the absence of long-range order. If we replace the right side of (12) by unity, we obtain a formula corresponding to random distribution of the four kinds of pairs, for given $R$, $Q$, and this would lead to the formulae of Bragg and Williams (zeroth approximation). We may reasonably expect the

* Chang, *Proc. Roy. Soc.* A, **173**, 48 (1939).

exponential factor on the right of (12) to be an improvement in the right direction over the zeroth approximation. However, our approximation can be justified better at a later stage. We shall see in § 1323 that formula (12), and formula (5) for that matter, can be derived from an entirely different method of approximation due to Bethe.

Formula (11) being a quadratic equation for $X$ can be solved, giving $X$ as an explicit function of $R$, $Q$ and $w/kT$. From here onwards we shall, however, confine ourselves to the simple case $R+Q = \frac{1}{2}N^l$. The more general case can be treated in precisely the same way, but the formulae are longer. For the simple case equation (11) reduces to

$$(R-X)(\tfrac{1}{2}N^l - R - X) = X^2 e^{2w/zkT}, \qquad (1317,13)$$

with the solution

$$\frac{X}{\frac{1}{2}N^l} = \frac{\{1+4R(\frac{1}{2}N^l - R)(e^{2w/zkT}-1)/\frac{1}{2}N^l\}^{\frac{1}{2}} - 1}{2(e^{2w/zkT}-1)}. \qquad (1317,14)$$

We can now return to our previous notation by substituting

$$R = \tfrac{1}{2}N^l\,\tfrac{1}{2}(1+s), \qquad (1317,15)$$

when (14) becomes

$$\frac{X}{\frac{1}{2}N^l} = \frac{\{1+(1-s^2)(e^{2w/zkT}-1)\}^{\frac{1}{2}} - 1}{2(e^{2w/zkT}-1)} = \frac{\frac{1}{2}(1-s^2)}{\{1+(1-s^2)(e^{2w/zkT}-1)\}^{\frac{1}{2}}+1}. \qquad (1317,16)$$

When $R+Q = \frac{1}{2}N^l$ formula (1) reduces to

$$W(R,X) = -N^l\chi_{AB} + 2Xw. \qquad (1317,17)$$

But according to the present approximation the average value of $X$ for given $R$ (that is given $s$) is determined by (16). Hence combining (16) with (17), we have

$$\overline{W}(s) = -N^l\chi_{AB} + \tfrac{1}{2}N^l w\frac{1-s^2}{\{1+(1-s^2)(e^{2w/zkT}-1)\}^{\frac{1}{2}}+1}. \qquad (1317,18)$$

We note that

$$\overline{W}(1) = -N^l\chi_{AB}; \quad W(0) = -N^l\chi_{AB} + \frac{\frac{1}{2}N^l w}{e^{w/zkT}+1}. \qquad (1317,19)$$

The configurational energy $E(s)$ is therefore given by

$$E(s)-E(1) = \overline{W}(s) - \overline{W}(1) = \tfrac{1}{2}N^l w\frac{1-s^2}{\{1+(1-s^2)(e^{2w/zkT}-1)\}^{\frac{1}{2}}+1}. \qquad (1317,20)$$

According to (1313, 11) the value of $\overline{\overline{W}}(s)$, corresponding to that of $\overline{W}(s)$ given by (18), is given by

$$\frac{\overline{\overline{W}}(s)}{\frac{1}{2}N^l} = -2\chi_{AB} + \tfrac{1}{2}w + \tfrac{1}{2}zkT\int_0^{2w/zkT}\frac{1-s^2}{\{1+(1-s^2)(e^{2w/zkT}-1)\}^{\frac{1}{2}}+1}\,d\left(\frac{2w}{zkT}\right), \qquad (1317,21)$$

the integration constant being determined by the condition $\overline{W}(s) \to \overline{W}(0)$ as $w/kT \to 0$.

If we use the substitution

$$\alpha = \{1 + (1 - s^2)(e^{2w/zkT} - 1)\}^{\frac{1}{2}}, \qquad (1317, 22)$$

we can simplify the integral in (20), and obtain

$$\frac{\overline{W}(s)}{\frac{1}{2}N^l kT} = \frac{-2\chi_{AB} + \frac{1}{2}w}{kT} + \frac{z}{2}\left\{(1+s)\log\frac{\alpha+s}{1+s} + (1-s)\log\frac{\alpha-s}{1-s} - 2\log\frac{\alpha+1}{2}\right\}. \qquad (1317, 23)$$

Using formula (1313, 4) for the case $x_A = x_B = \frac{1}{2}$ together with (23), we obtain for the configurational free energy according to (1313, 9)

$$\frac{F(s)}{\frac{1}{2}N^l kT} = \frac{-2\chi_{AB} + \frac{1}{2}w}{kT} + (1+s)\log(1+s) + (1-s)\log(1-s) - 2\log 2$$
$$+ \frac{z}{2}\left\{(1+s)\log\frac{\alpha+s}{1+s} + (1-s)\log\frac{\alpha-s}{1-s} - 2\log\frac{\alpha+1}{2}\right\}. \qquad (1317, 24)$$

In particular, when $s = 1$, we have $\alpha = 1$ and (24) reduces to

$$\frac{F(1)}{\frac{1}{2}N^l kT} = \frac{-2\chi_{AB} + \frac{1}{2}w}{kT}, \qquad (1317, 25)$$

so that we can rewrite (24) as

$$\frac{F(s) - F(1)}{\frac{1}{2}N^l kT} = (1+s)\log(1+s) + (1-s)\log(1-s) - 2\log 2$$
$$+ \frac{z}{2}\left\{(1+s)\log\frac{\alpha+s}{1+s} + (1-s)\log\frac{\alpha-s}{1-s} - 2\log\frac{\alpha+1}{2}\right\}. \qquad (1317, 26)$$

We can expand the logarithms in powers of $(\alpha - 1)$ and then expand $\alpha$ in powers of $w/kT$. We obtain finally

$$\frac{F(s) - F(1)}{\frac{1}{2}N^l kT} = (1+s)\log(1+s) + (1-s)\log(1-s) - 2\log 2$$
$$+ \frac{w}{kT}\left\{\tfrac{1}{2}(1-s^2) - \frac{w}{zkT}\tfrac{1}{8}(1-s^2)^2 - \left(\frac{w}{zkT}\right)^2 \tfrac{1}{12}s^2(1-s^2)^2 + \ldots\right\}, \qquad (1317, 27)$$

which agrees with Kirkwood's formula (5) as far as the highest terms there included. We conclude that the present method, which depends on the arbitrary assumption (3) or (5), leads to results accurate at least as far as terms in $F(s)$ of the order $(w/zkT)^2$. The zeroth approximation used by Bragg and Williams is obtained by ignoring the terms in $w/zkT$ and higher powers. We can therefore formally obtain their zeroth approximation by letting $z \to \infty$. The dependence of $F(s)$ on $s$ according to formula (26) is generally similar to that shown in Fig. 5.

By differentiating (26) with respect to $s$, we obtain

$$\frac{\partial F/\partial s}{\frac{1}{2}N^l kT} = \frac{2-z}{2}\log\frac{1+s}{1-s}+\frac{z}{2}\log\frac{\alpha+s}{\alpha-s}, \qquad (1317, 28)$$

the remaining terms cancelling. The equilibrium value of $s$ is therefore determined by

$$\log\frac{\alpha+s}{\alpha-s} = \frac{z-2}{z}\log\frac{1+s}{1-s}. \qquad (1317, 29)$$

The dependence of this equilibrium value of $s$ on the temperature is shown in Fig. 6.

The Curie temperature is determined, as we have seen, by the conditions (1316, 7). Differentiating (28) with respect to $s$, we find

$$\frac{\partial^2 F/\partial s^2}{\frac{1}{2}N^l kT} = -\frac{z-2}{1-s^2}+\frac{z}{\alpha(1-s^2)}. \qquad (1317, 30)$$

The equations (1316, 7) are therefore satisfied by $s = 0$ and

$$z/(z-2) = \alpha = e^{w/zkT_c}, \qquad (1317, 31)$$

which can be rewritten as

$$\frac{w}{kT_c} = z\log\frac{z}{z-2}. \qquad (1317, 32)$$

We observe that if we expand (31) in powers of $w/zkT_c$, the first four terms agree with Kirkwood's formula (1316, 9), while if we retain only the first two terms we obtain Bragg and Williams' formula (1315, 7).

The configurational energy at any temperature not less than $T_c$ is obtained by putting $s = 0$ in (20). We thus obtain

$$E_{T\geqslant T_c} - E_{T=0} = \tfrac{1}{2}N^l\frac{w}{e^{w/zkT}+1}. \qquad (1317, 33)$$

In particular at the Curie temperature we have, using (32),

$$\frac{E_{T=T_c} - E_{T=0}}{N^l kT_c} = \frac{z(z-2)}{4(z-1)}\log\frac{z}{z-2}. \qquad (1317, 34)$$

**§ 1318. Résumé of methods of treatment.** It will be useful at this stage to recall the three methods of estimating the configurational free energy which we have already described, and to refer briefly to a fourth method which will be discussed in §§ 1321–1323.

Firstly, we have the method of Bragg and Williams which we shall refer to by the letters B.-W. This method may be regarded as a zeroth approximation to any of the other methods. The B.-W. formulae are in fact obtained from those of any of the more accurate methods by making $z\to\infty$.

Secondly, we have the method of Kirkwood, which we shall refer to by the

letter K., which gives formulae as power series in $w/zkT$. These formulae are accurate as far as the highest terms yet calculated.

Thirdly, we have the quasi-chemical method, which we shall refer to by the letters Q.-C. The method at this stage must be regarded as based on a guess. The formulae obtained agree with those obtained by the K. method up to the highest powers of $w/zkT$ yet evaluated.

The fourth method is due to Bethe and will be referred to by the letter B. We postpone description of it to a later stage because the method is less straightforward than any of the others. The method consists essentially in an approximate construction of the grand partition function for a small group of sites, in fact the method which we have already used in §§ 608 sqq. for assemblies without long-range order. We can the more readily postpone discussion of the method since, in spite of its widely different appearance, it is in fact mathematically equivalent to the Q.-C. method. The proof of this complete equivalence was first given by Chang.

For convenience of reference we collect the formulae for the critical temperature for an alloy of equal numbers of $A$ and $B$ atoms according to the several approximations

B.-W. $$1-\frac{2}{z} = 1-\frac{w}{zkT_c}; \qquad (1318,1)$$

K. $$1-\frac{2}{z} = 1-\frac{w}{zkT_c}+\frac{1}{2}\left(\frac{w}{zkT_c}\right)^2-\frac{1}{6}\left(\frac{w}{zkT_c}\right)^3+\ldots; \qquad (1318,2)$$

Q.-C. / B. $$1-\frac{2}{z} = e^{-w/zkT_c}. \qquad (1318,3)$$

We have not written every equation in its simplest form, but rather in such a form as to show its similarity to the others.

In the more general case $x_A \neq x_B$, the formula for the Curie temperature according to the Q.-C. or B. approximation has been derived by Easthope.* For convenience we shall quote it without giving the derivation and at the same time we given the B.-W. formula (1315, 6) in a form convenient for comparison with the more accurate formula.

B.-W. $$1-\frac{2w}{zkT_c} = 1-\frac{1}{x_A z}-\frac{1}{x_B z}, \qquad (1318,4)$$

Q.-C. or B. $$e^{-2w/zkT_c} = \frac{(x_A z-1)(x_B z-1)}{x_A z \,.\, x_B z}. \qquad (1318,5)$$

According to either formula the curve for $T_c$ against $x_A$ $(=1-x_B)$ is symmetrical about $x_A = x_B = \frac{1}{2}$ where it has a maximum.

* Easthope, *Proc. Camb. Phil. Soc.* **33**, 502 (1937).

**§ 1319. Anomalous heat capacity.** In the simplest case of $x_A = x_B = \frac{1}{2}$, the configurational energy $E(s)$, given by (1317, 20), can be expressed in the convenient form

$$E(s) - E(1) = \tfrac{1}{2} N^l w \frac{1 - s^2}{\alpha(s, T) + 1}, \qquad (1319, 1)$$

where $\alpha(s, T)$ is defined by

$$\alpha(s, T) = \{1 + (1 - s^2)(e^{2w/zkT} - 1)\}^{\frac{1}{2}}, \qquad (1319, 2)$$

and $s$ is determined by equation (1317, 29). By solving this equation numerically for various values of $T$ and substituting into (1), we obtain the curve in Fig. 7. The configurational contribution to the atomic heat capacity is given by the slope of this curve. We observe that as the Curie temperature is passed there is a sudden fall in the heat capacity, but it does not fall to zero. The contribution to the heat capacity per atom is

$$C = \frac{1}{N^l} \frac{dE(s)}{dT} = \tfrac{1}{2} w \frac{d}{dT} \left\{ \frac{1 - s^2}{\alpha(s, T) + 1} \right\}$$

$$= \frac{1}{2} \frac{w}{\alpha + 1} \left\{ - \frac{1}{\alpha + 1} \frac{\partial \alpha}{\partial T} - \frac{1}{\alpha + 1} \frac{\partial \alpha}{\partial s^2} \frac{ds^2}{dT} - \frac{ds^2}{dT} \right\}. \qquad (1319, 3)$$

The values of $\partial\alpha/\partial T$ and $\partial\alpha/\partial s^2$ are obtainable directly from (2), while that of $ds^2/dT$ can be obtained by differentiating (1317, 29). Thus the value of $C$ can be calculated for any temperature $T$ as a function of $T$, $s$, the value of $s$ being determined by (1317, 29). The result of this calculation is shown in Fig 8 for $z = 6$ and for $z = \infty$, the latter being equivalent to the B.-W. approximation We cannot obtain a simple formula for $C$ as an explicit function of $T$ only. We can, however, obtain such formulae for $C$ in the immediate neighbourhood of the Curie temperature $T_c$. This temperature region is of particular interest because as we shall see there is a discontinuity in $C$ at the temperature $T_c$, due to the sudden vanishing of $ds^2/dT$ when $T$ becomes greater than $T_c$. We shall now obtain these formulae.

Our first step is to determine the dependence of $s$ on $T$ for temperatures slightly below $T_c$. From Fig. 6 we notice that $ds/dT \to \infty$ as $T \to T_c - 0$. It can be verified that $ds/dT$ becomes infinite like $-1/s$, so that $ds^2/dT$ remains finite. This is the reason we use the variable $s^2$ rather than $s$. Since the critical temperature is given by (1317, 31) we assume that at temperatures just below $T_c$ we have

$$e^{w/zkT} = \frac{z}{z - 2}(1 + \lambda s^2 + \ldots), \qquad (1319, 4)$$

where for the present purpose we are not interested in powers of $s$ higher than $s^2$. Substituting from (4) into (2) and neglecting higher powers of $s$, we obtain

$$\alpha \sim \frac{z}{z - 2} \left\{ 1 + s^2 \left( \lambda - \frac{2z - 2}{z^2} \right) \right\}, \qquad (1319, 5)$$

and consequently

$$\frac{z}{2s(z-2)}\log\frac{\alpha+s}{\alpha-s}\sim 1-s^2\left(\lambda-\frac{2z-2}{z^2}-\frac{1}{3}\frac{[z-2]^2}{z^2}\right). \qquad (1319,6)$$

To the same order of approximation we have

$$\frac{1}{2s}\log\frac{1+s}{1-s}\sim 1+\tfrac{1}{3}s^2. \qquad (1319,7)$$

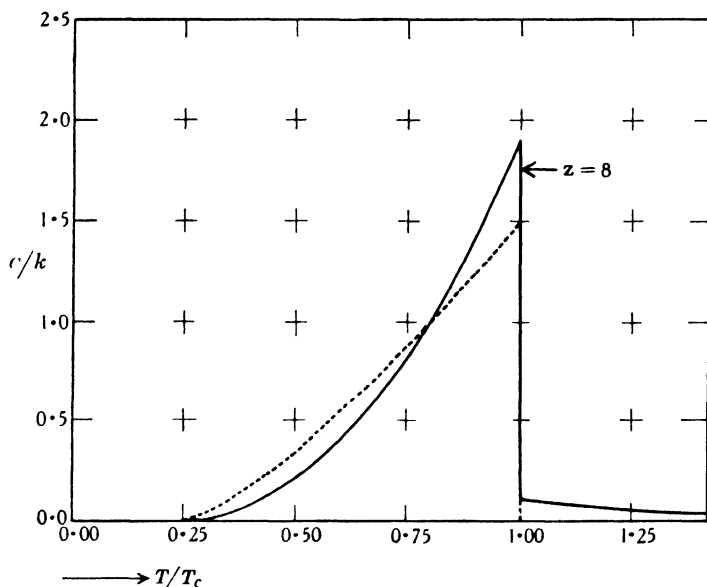



Fig. 8. Theoretical configurational contribution to atomic heat capacity of $\beta$-brass.
·········· B.-W. approximation. ———— B or Q.-C. approximation for $z = 6$.
The Q.-C. curve for $z = 8$ will be intermediate between the two curves drawn, and will rise to the point marked with an arrow.

Substituting from (6) and (7) into the equilibrium relation (1317, 29) between $s$ and $T$, and equating the coefficients of $s^2$, we obtain

$$\lambda-\frac{2z-2}{z^2}-\frac{1}{3}\frac{(z-2)^2}{z^2}=-\frac{1}{3}, \qquad (1319,8)$$

which reduces to

$$\lambda=\frac{2(z-1)}{3z^2}. \qquad (1319,9)$$

Differentiating (4) with respect to $T$, using (1317, 31) and (9), and letting $T\to T_c-0$, we obtain finally

$$T\frac{ds^2}{dT}\sim-\frac{3z^2}{2(z-1)}\log\frac{z}{z-2}\quad (T\to T_c-0). \qquad (1319,10)$$

By differentiating (2) partially, letting $T' \to T_c$ and using (1317, 31) and (10), we obtain

$$\left(\frac{\partial \alpha}{\partial s^2}\right)_T \sim -\frac{2(z-1)}{z(z-2)} \quad (T \to T_c), \tag{1319, 11}$$

$$T\left(\frac{\partial \alpha}{\partial T}\right)_s \sim -\frac{z}{z-2} \log \frac{z}{z-2} \quad (T \to T_c). \tag{1319, 12}$$

When we substitute from (10), (11) and (12) into (3) and use (1317, 31), we obtain

$$\frac{C_{T_c-0}}{k} = \frac{z-2}{8}\left(\frac{z}{z-1}\right)^2 \left(\log \frac{z}{z-2}\right)^2 \times (3z-2). \tag{1319, 13}$$

At temperatures above $T_c$ we have $s = 0$ and $ds^2/dT = 0$, and formula (3) reduces to its first term. Using the value of $(\partial\alpha/\partial T)_s$ given by (12), we find

$$\frac{C_{T_c+0}}{k} = \frac{z-2}{8}\left(\frac{z}{z-1}\right)^2 \left(\log \frac{z}{z-2}\right)^2. \tag{1319, 14}$$

By comparison of (13) and (14) we see that $C$ jumps by a factor $3z-2$ as the critical temperature is passed. Inserting the value $z = 8$ into (13) and (14), we obtain

$$C_{T_c-0}/k = 1{\cdot}78, \quad C_{T_c+0}/k = 0{\cdot}081 \quad (z=8). \tag{1319, 15}$$

For comparison with other methods of approximation it is convenient to subtract (14) from (13); we obtain

$$\frac{C_{T_c-0} - C_{T_c+0}}{k} = \frac{3}{8}\frac{z-2}{z-1}\left(z \log \frac{z}{z-2}\right)^2, \tag{1319, 16}$$

which, by using (1317, 32), we can rewrite in the form

$$\frac{C_{T_c-0} - C_{T_c+0}}{\frac{3}{2}k}\left(\frac{2kT_c}{w}\right)^2 = \frac{z-2}{z-1} = 1 - \frac{1}{z} - \frac{1}{z^2} - \frac{1}{z^3} - \dots. \tag{1319, 17}$$

The B.-W. approximation is obtained by replacing the right side of (17) by unity. The K. approximation leads to the formula

$$\frac{C_{T_c-0} - C_{T_c+0}}{\frac{3}{2}k}\left(\frac{2kT_c}{w}\right)^2 = 1 - \frac{1}{z} - \frac{1}{z^2} + O\left(\frac{1}{z^3}\right), \tag{1319, 18}$$

and so agrees with the Q.-C. or B. formula (16) as far as the highest terms calculated by the K. method. If we retain in (18) only one term beyond the B.-W. approximation, we have

$$\frac{C_{T_c-0} - C_{T_c+0}}{\frac{3}{2}k}\left(\frac{2kT_c}{w}\right)^2 \simeq 1 - \frac{1}{z}. \tag{1319, 19}$$

When $z = 6$ the right side of (17) is 0·800, while the right side of (19) is 0·833. Thus we see that (19) appears to be a fairly good approximation to (17), but in spite of this agreement the convergence of the K. series is not sufficiently rapid to justify the retention of only one term beyond the B.-W. approxima-

tion. The danger of such a procedure may be illustrated by the following considerations. Kirkwood actually used the formula

$$\frac{C_{T_c-0}-C_{T_c+0}}{\frac{3}{2}k}\left(\frac{2kT_c}{w}\right)^2 \simeq \left\{1-\frac{2}{z}\frac{w}{2kT_c}\right\}^2 \left\{1-\frac{3}{z}\left(\frac{w}{2kT_c}\right)^2\right\}^{-1}. \quad (1319, 20)$$

Since according to the B.-W. approximation $w/2kT_c = 1$, formula (20) is equivalent to (19) as far as terms in $z^{-1}$, that is to say, as far as the highest terms that are significant, but (20) contains spurious higher order terms. The value of $w/2kT_c$ for $z = 6$ according to the present approximation is 1·27 and the right side of (20) is therefore 1·70 as compared with the value 0·833 for the right side of (19). If, however, we replace the factors $w/2kT_c$ on the right side of (20) by unity, their value according to the zeroth approximation, the right side becomes reduced to 0·889. Thus we see that the particular form (20) leads to spuriously high values for the jump in the heat capacity, although it is formally correct to the same order as (19), which is a good approximation to the more accurate formula (17).

§ **1320. Comparison with experiment.** We shall now consider briefly the comparison between the theoretical results of the foregoing sections and such suitable experimental data as are available.

The configurational energy content during the changes of ordering can be determined calorimetrically, provided that care be taken to ensure that the equilibrium state of order is reached at each temperature, a process which may be slow. The danger of allowing insufficient time for complete equilibrium to be established is particularly great in this field; by sufficiently rapid cooling (quenching) most alloys, which possess an ordered equilibrium state at low temperatures, can be brought to low temperatures in a more or less completely disordered state and retained thus indefinitely in a metastable equilibrium. It is moreover undoubtedly correct to hold the view that many other alloys, not known to occur in an ordered state at low temperatures, are really frozen in a metastable disordered state, because the temperature at which changes of position in the lattice ceases to be possible at reasonable speed is higher than the Curie temperature for the order-disorder transition. The rate of attainment of order has been discussed by Bragg and Williams* and Nix and Shockley,† but further discussion of it lies outside the field of this book.

The alloy of Zn and Cu known as $\beta$-brass is particularly suitable for comparison between theory and experiment, because in the neighbourhood of the Curie temperature equilibrium is attained rapidly. This is proved by the fact that the observed values of the heat capacity with rising and with falling

* Bragg and Williams, *Proc. Roy. Soc.* A, **145**, 699 (1934).
† Nix and Shockley, *Rev. Mod. Phys.* **10**, 1 (1938).

temperatures agree with each other. The phase range of $\beta$-brass extends only between the atomic fractions 0·458 and 0·489 of Zn. Thus the composition CuZn is just outside the range, but the deviation from the 1 : 1 ratio may be neglected. The superlattice structure of this alloy has been established by X-ray measurements by Jones and Sykes.* In the ordered arrangements each Cu atom has eight neighbours all Zn atoms, and vice versa, as shown in Fig. 4*a*. The order-disorder Curie temperature is 742° K. Accurate measurements of the heat capacity have been made by Sykes and

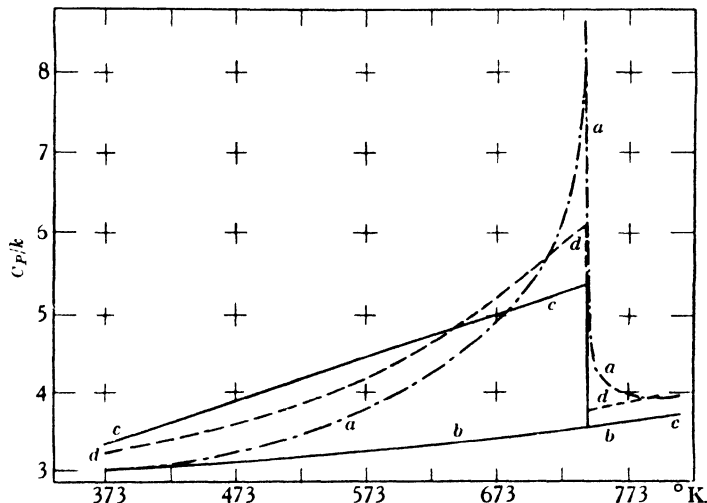



Fig. 9. Heat capacity (per atom) of CuZn. *a*, Experimental for CuZn (Sykes and Wilkinson). *b*, Mean of experimental curves for pure Cu and pure Zn. *c*, Calculated on zeroth approximation (B.-W.). *d*, Calculated by B. or Q.-C. method for $z = 6$.

The required curve for $z = 8$ will be intermediate between curves *c* and *d*, about one-quarter the way from *d* towards *c*.

Wilkinson† and independently by Moser.‡ The two sets of measurements are in strikingly good agreement with each other. Comparison of the data of Sykes and Wilkinson with the theory is made in Fig. 9. Curve *a* represents the experimental data for $C_P$ in an alloy with an atomic fraction 0·490 zinc. This has to be compared with a theoretical curve constructed by adding the theoretical configurational heat capacity to the mean of the experimental $C_P$ curves for Cu and for Zn, curve *b* in the diagram. By this procedure one obtains curve *c* on the B.-W. approximation, and curve *d* on the Q.-C. or B. approximation for $z = 6$. The required curve for $z = 8$ on the Q.-C. or B.

* Jones and Sykes, *Proc. Roy. Soc.* A, **161**, 440 (1937).
† Sykes and Wilkinson, *J. Inst. Metals*, **61**, 223 (1937).
‡ Moser, *Physikal. Zeit.* **37**, 737 (1936).

approximation will be intermediate between curves $c$ and $d$ and approximately one-quarter the way from the curve for $z = 6$ to the B.-W. curve. We see that qualitatively the experimental curve agrees with that of the first approximation (B. or Q.-C.), but there is no quantitative agreement. The maximum configurational heat capacity per atom observed is $5{\cdot}1k$, as compared with the calculated values $1{\cdot}50k$ according to the B.-W. approximation and $1{\cdot}78k$ according to the B. or Q.-C. approximation. It is clear that the energy changes associated with the disappearance of order are more closely concentrated around the Curie temperature than is predicted by the theory.

There is thus a real discrepancy between the theory and experiment which may be due to any of several causes such as

(1) neglect of interactions between atoms not nearest neighbours,*

(2) neglect of dependence of $w$ on interatomic distance which alters with temperature,†

(3) neglect of the electronic structure which may be quite different in an alloy from that in the simple metals.‡

Each one of these causes can be shown to make the disappearance of order more sudden than predicted above, but the reader interested in these elaborations of the theory must consult the papers, to which we give references.

The discrepancy between theory and experiment is naturally less obvious, if instead of comparing heat capacities we compare the energy change over a wide temperature range; that is to say, if we compare the integrals of the heat capacity. The most suitable temperature range for the comparison is from a temperature so low that order is effectively complete up to the Curie temperature. The configurational energy increase in this range is given by formula (1317, 34), which for $z = 8$ becomes

$$\frac{E_{T_c} - E_{T=0}}{N^l k T_c} = 0{\cdot}49_2,$$

while the zeroth approximation (B.-W.) gives the value 0·50. The experimental value, given by the area between the curves $a$ and $b$ in Fig. 9 to the left of $T = T_c$, is 0·43.

Since we have no *a priori* knowledge of the value of $w$, only those relations can be compared with experiment from which $w$ has been eliminated. The dependence of the Curie temperature on the composition is thus suitable

* See Chang, *Proc. Roy. Soc.* A, **161**, 546 (1937).

† See Eisenschitz, *Proc. Roy. Soc.* A, **168**, 546 (1938).

‡ See Mott, *Proc. Phys. Soc.* **49**, 258 (1937).

for comparison. The experimental data of Sykes and Wilkinson* for CuZn are compared with theory in Fig. 10*a*. The B.-W. approximation is given by formula (1315, 6) and the Q.-C. or B. approximation† by formula (1318, 5).

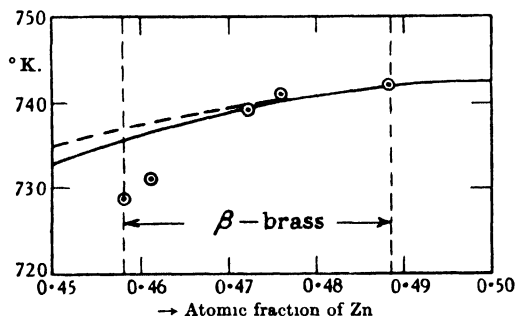



Fig. 10*a*. Curie temperature of β-brass

⊙ Experimental (Sykes and Wilkinson). - - - - - - - Calculated (B.-W.).
——— Calculated (B. or Q.-C.).

The agreement between the experimental data and the latter is moderate. We can also use the data on $Fe_3Al$ for comparison between theory and experiment. This alloy is effectively an example of a superlattice with a 1 : 1 ratio of *a* and *b* sites, because, as shown in Fig. 4*b*, all the cube corners are permanently occupied by Fe atoms and only the cube centres are involved in an order-disorder arrangement of Fe and Al atoms. The experimental data of Sykes‡ are compared with the theoretical curve in Fig. 10*b*. The experimental points are consistent with the theoretical curve.

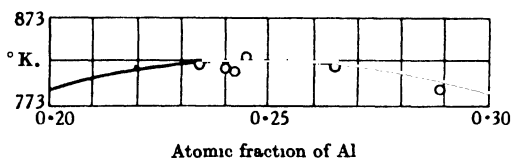



Fig. 10*b*. Curie temperature of $Fe_3Al$ and neighbouring compositions.

**§ 1321. Grand partition functions for groups of sites (Bethe).** We shall now describe the (apparently) quite distinct method of approximation introduced by Bethe.§ In § 608 we approximated to the grand partition functions for what we there called regular assemblies by the method of con-

* Sykes and Wilkinson, *J. Inst. Metals*, **61**, 223 (1937). This paper contains an excellent review of the equilibrium properties of β-brass.

† The theoretical curve obtained by the B. method is drawn incorrectly by Nix and Shockley in their Fig. 39, *Rev Mod. Phys.* **10**, 46 (1938).

‡ Sykes, see Bragg and Williams, *Proc. Roy. Soc.* A, **151**, 540 (1935).

§ Bethe, *Proc. Roy. Soc.* A, **150**, 552 (1935).

structing grand partition functions for small groups of sites, using mean values for the factors contributed by the other sites. For such regular assemblies all sites may be assumed to have identical average properties. In the order-disorder problem, on the other hand, it is of the essence of the problem that there are two classes of sites, *a* sites and *b* sites, and the method must be generalized accordingly. We shall continue to confine attention to *ab* lattices in which all the nearest neighbours of *a* sites are *b* sites and vice versa; also to make the assumption, characteristic of any regular assembly, that the configurational energy is composed solely of the interaction of pairs of nearest neighbours.* The energy $W_\tau$ of a configurational state $\tau$ is then of the form (1313, 12). We shall find it is convenient to work as in Chapter VI, with the grand partition function, but we shall concern ourselves only with the contribution of the configurational factors. We, therefore, may write in place of (608, 3)

$$\Gamma(T, \lambda_A, \lambda_B) = \Sigma_{(N_A)} \Sigma_{(n_{AB})} g(N_A, \ldots, n_{AB}, \ldots)\, e^{\Sigma 2 n_{AB}\chi_{AB}/zkT}\, \lambda_A^{N_A} \lambda_B^{N_B}. \tag{1321, 1}$$

The factors $\phi_A, \ldots$ of (608, 3) dealing with the excited states of a given system $A$ in any configuration may here be omitted. In the absence of an adequate knowledge of $g(N_A, \ldots, n_{AB}, \ldots)$ we wish to approximate to the exact expression (1), by elaborating the procedure of § 608.

We shall work primarily with an approximation corresponding to that called $\Xi_{z+1}$ in § 608, although the work can equally well be carried through by using the approximation $\Xi_2$, but it then corresponds less closely to the methods actually used by Bethe. Using the notation of equation (1) we assume that we can approximate to $\Gamma$ by finding its maximum term, $N_A^*, \ldots, n_{AB}^*, \ldots$, and writing it in either of the equivalent forms

$$\Gamma = \Gamma^* = \gamma^{N^l} \xi^{N^l} \eta^{\frac{1}{2}zN^l}, \tag{1321, 2}$$

$$\Gamma = \Gamma_{z+1} = \{\lambda_A(\lambda_A \eta_{AA} \eta_A^{z-1} + \lambda_B \eta_{AB} \eta_B^{z-1})^z + \lambda_B(\lambda_A \eta_{AB} \eta_A^{z-1} + \lambda_B \eta_{BB} \eta_B^{z-1})^z\} \times \gamma^{N^l - z - 1} \xi^{N^l - z - 1} \eta^{\frac{1}{2}zN^l - z^2}. \tag{1321, 3}$$

The $\gamma$, $\xi$, $\eta$, $\eta_A$, $\eta_B$ are suitably defined mean values, of which $\eta_A$, $\eta_B$ are parameters fixed by a condition of consistency of the representation. The remaining symbols $\eta_{AA}, \ldots$ are defined by

$$\eta_{AA} = e^{2\chi_{AA}/zkT}, \ldots. \tag{1321, 4}$$

The properties of regular assemblies were derived from these approximate grand partition functions by requiring that the nature of the occupation of every site in the assembly should be the same. For this purpose the factor

* These rather stringent restrictions can be removed. Those interested should consult Peierls, *Proc. Roy. Soc.* A, **154**, 207 (1936) and Chang, *Proc. Roy. Soc.* A, **161**, 546 (1937).

$\gamma^{Nl-z-1}\xi^{Nl-z-1}\eta^{\frac{1}{2}zNl-z^2}$ is irrelevant and may conveniently be omitted. We therefore replace (3) by the simpler expression

$$\Gamma = \Gamma_{z+1} = \lambda_A(\lambda_A\eta_{AA}\epsilon_A+\lambda_B\eta_{AB}\epsilon_B)^z+\lambda_B(\lambda_A\eta_{AB}\epsilon_A+\lambda_B\eta_{BB}\epsilon_B)^z, \tag{1321, 5}$$

where for brevity we have replaced $\eta_A^{z-1}$ by $\epsilon_A$ and $\eta_B^{z-1}$ by $\epsilon_B$.

We can proceed in almost the same way in dealing with assemblies with long-range order, as for regular assemblies, merely remembering to distinguish between $a$ sites and $b$ sites. For a group of a central site $a$ with $z$ neighbouring $b$ sites we write

$$\Gamma^a = \gamma_A^a+\gamma_B^a = \lambda_A(\lambda_A\eta_{AA}\epsilon_A^b+\lambda_B\eta_{AB}\epsilon_B^b)^z+\lambda_B(\lambda_A\eta_{AB}\epsilon_A^b+\lambda_B\eta_{BB}\epsilon_B^b)^z, \tag{1321, 6}$$

where $\epsilon_A^b$ allows for the interaction between an $A$ atom on an outer $b$ site with the rest of the assembly, and $\epsilon_B^b$ for that between a $B$ atom on an outer $b$ site with the rest of the assembly. The terms $\gamma_A^a$ and $\gamma_B^a$, defined by

$$\gamma_A^a = \lambda_A(\lambda_A\eta_{AA}\epsilon_A^b+\lambda_B\eta_{AB}\epsilon_B^b)^z, \tag{1321, 7}$$

$$\gamma_B^a = \lambda_B(\lambda_A\eta_{AB}\epsilon_A^b+\lambda_B\eta_{BB}\epsilon_B^b)^z, \tag{1321, 8}$$

correspond respectively to configurations in which the atom on the central site is $A$ or $B$. Actually, since only ratios of any terms are significant for the present purpose, it turns out not to be necessary to include both $\epsilon_A^b$ and $\epsilon_B^b$; actually Bethe put $\epsilon_B^b = 1$.

The corresponding $\Gamma^b$ for a group of a central site $b$ with $z$ neighbouring sites $a$ is in corresponding notation

$$\Gamma^b = \gamma_A^b+\gamma_B^b = \lambda_A(\lambda_A\eta_{AA}\epsilon_A^a+\lambda_B\eta_{AB}\epsilon_B^a)^z+\lambda_B(\lambda_A\eta_{AB}\epsilon_A^a+\lambda_B\eta_{BB}\epsilon_B^a)^z. \tag{1321, 9}$$

For the internal consistency of (6) and (9) it is necessary that they should lead to the same value for the frequency of occupation of a central $a$ site by an $A$ atom and for the frequency of occupation of an outer $a$ site by an $A$ atom; and likewise for a central $b$ site and an outer $b$ site. By the standard properties of grand partition functions these conditions of self-consistency are

$$\frac{\gamma_A^a}{\gamma_A^a+\gamma_B^a} = \frac{\lambda_A\eta_{AA}\epsilon_A^a}{\lambda_A\eta_{AA}\epsilon_A^a+\lambda_B\eta_{AB}\epsilon_B^a}\,\frac{\gamma_A^b}{\gamma_A^b+\gamma_B^b}+\frac{\lambda_A\eta_{AB}\epsilon_A^a}{\lambda_A\eta_{AB}\epsilon_A^a+\lambda_B\eta_{BB}\epsilon_B^a}\,\frac{\gamma_B^b}{\gamma_A^b+\gamma_B^b}, \tag{1321, 10}$$

$$\frac{\gamma_B^b}{\gamma_A^b+\gamma_B^b} = \frac{\lambda_B\eta_{AB}\epsilon_B^b}{\lambda_A\eta_{AA}\epsilon_A^b+\lambda_B\eta_{AB}\epsilon_B^b}\,\frac{\gamma_A^a}{\gamma_A^a+\gamma_B^a}+\frac{\lambda_B\eta_{BB}\epsilon_B^b}{\lambda_A\eta_{AB}\epsilon_A^b+\lambda_B\eta_{BB}\epsilon_B^b}\,\frac{\gamma_B^a}{\gamma_A^a+\gamma_B^a}. \tag{1321, 11}$$

If we continue to define the long-range order $s$ so that the numbers of $A$ atoms on $a$ sites, etc. are as given in Table 3, then the equilibrium value of

the long-range order is related to the ratios of the $\gamma$'s by the equations:

$$\gamma_A^a/(\gamma_A^a+\gamma_B^a) = x_A + x_A s, \quad \gamma_B^a/(\gamma_A^a+\gamma_B^a) = x_B - x_A s, \qquad (1321, 12)$$

$$\gamma_A^b/(\gamma_A^b+\gamma_B^b) = x_A - x_A s, \quad \gamma_B^b/(\gamma_A^b+\gamma_B^b) = x_B + x_A s. \qquad (1321, 13)$$

Substituting from (12) and (13) into (10) and (11), we obtain

$$x_A + x_A s = \frac{\lambda_A \eta_{AA} \epsilon_A^a (x_A - x_A s)}{\lambda_A \eta_{AA} \epsilon_A^a + \lambda_B \eta_{AB} \epsilon_B^a} + \frac{\lambda_A \eta_{AB} \epsilon_A^a (x_B + x_A s)}{\lambda_A \eta_{AB} \epsilon_A^a + \lambda_B \eta_{BB} \epsilon_B^a}, \qquad (1321, 14)$$

$$x_B + x_A s = \frac{\lambda_B \eta_{AB} \epsilon_B^b (x_A + x_A s)}{\lambda_A \eta_{AA} \epsilon_A^b + \lambda_B \eta_{AB} \epsilon_B^b} + \frac{\lambda_B \eta_{BB} \epsilon_B^b (x_B - x_A s)}{\lambda_A \eta_{AB} \epsilon_A^b + \lambda_B \eta_{BB} \epsilon_B^b}. \qquad (1321, 15)$$

By combining equations (7) and (8) with the analogous definitions of $\gamma_A^b$ and $\gamma_B^b$, we obtain

$$\frac{\gamma_A^b \gamma_B^a}{\gamma_A^a \gamma_B^b} = \left\{\frac{(\lambda_A \eta_{AA} \epsilon_A^a + \lambda_B \eta_{AB} \epsilon_B^a)(\lambda_A \eta_{AB} \epsilon_A^b + \lambda_B \eta_{BB} \epsilon_B^b)}{(\lambda_A \eta_{AA} \epsilon_A^b + \lambda_B \eta_{AB} \epsilon_B^b)(\lambda_A \eta_{AB} \epsilon_A^a + \lambda_B \eta_{BB} \epsilon_B^a)}\right\}^s. \qquad (1321, 16)$$

Substituting from (12) and (13) into (16), we deduce

$$\frac{(x_A - x_A s)(x_B - x_A s)}{(x_A + x_A s)(x_B + x_A s)} = \left\{\frac{(\lambda_A \eta_{AA} \epsilon_A^a + \lambda_B \eta_{AB} \epsilon_B^a)(\lambda_A \eta_{AB} \epsilon_A^b + \lambda_B \eta_{BB} \epsilon_B^b)}{(\lambda_A \eta_{AA} \epsilon_A^b + \lambda_B \eta_{AB} \epsilon_B^b)(\lambda_A \eta_{AB} \epsilon_A^a + \lambda_B \eta_{BB} \epsilon_B^a)}\right\}^z. \qquad (1321, 17)$$

We shall find that equations (14), (15), and (17) suffice for the determination of the equilibrium value of $s$ in terms of known quantities.

We can also write down formulae for $\overline{n_{AA}}$, $\overline{n_{BB}}$, $\overline{n_{AB}}$ from the known properties of the grand partition functions. Actually it is sufficient to have a formula for any one of these quantities since the other two are then fixed by the necessary equalities

$$2\overline{n_{AA}} + \overline{n_{AB}} = zN_A, \quad 2\overline{n_{BB}} + \overline{n_{AB}} = zN_B. \qquad (1321, 18)$$

We shall therefore consider only the formula for $\overline{n_{AB}}$. Actually we can obtain two such formulae according as we use $\Gamma^a$ or $\Gamma^b$. From the known properties of $\Gamma^a$ we have

$$\frac{\overline{n_{AB}}}{\frac{1}{2}zN^l} = \frac{\gamma_A^a}{\gamma_A^a+\gamma_B^a} \frac{\lambda_B \eta_{AB} \epsilon_B^b}{\lambda_A \eta_{AA} \epsilon_A^b + \lambda_B \eta_{AB} \epsilon_B^b} + \frac{\gamma_B^a}{\gamma_A^a+\gamma_B^a} \frac{\lambda_A \eta_{AB} \epsilon_A^b}{\lambda_A \eta_{AB} \epsilon_A^b + \lambda_B \eta_{BB} \epsilon_B^b}$$

$$= \frac{(x_A + x_A s)\lambda_B \eta_{AB} \epsilon_B^b}{\lambda_A \eta_{AA} \epsilon_A^b + \lambda_B \eta_{AB} \epsilon_B^b} + \frac{(x_B - x_A s)\lambda_A \eta_{AB} \epsilon_A^b}{\lambda_A \eta_{AB} \epsilon_A^b + \lambda_B \eta_{BB} \epsilon_B^b}. \qquad (1321, 19)$$

Similarly from the known properties of $\Gamma^b$ we have

$$\frac{\overline{n_{AB}}}{\frac{1}{2}zN^l} = \frac{(x_A - x_A s)\lambda_B \eta_{AB} \epsilon_B^a}{\lambda_A \eta_{AA} \epsilon_A^a + \lambda_B \eta_{AB} \epsilon_B^a} + \frac{(x_B + x_A s)\lambda_A \eta_{AB} \epsilon_A^a}{\lambda_A \eta_{AB} \epsilon_A^a + \lambda_B \eta_{BB} \epsilon_B^a}. \qquad (1321, 20)$$

The mutual consistency of (19) and (20) is in fact guaranteed by equations (14) and (15), as we shall verify in the next section.

These are the general formulae of Bethe's theory, constructed in complete detail, so that it may be seen that allowance is made for every interaction which the theory purports to take into account.

**§ 1322. Development of Bethe's equations.** From the point of view of rapid working the equations derived in detail in the preceding section contain much lumber which can now be removed. Equations (1321, 14), (1321, 15) and (1321, 17) really contain only two unknown ratios $\lambda_A \epsilon_A^a / \lambda_B \epsilon_B^a$ and $\lambda_A \epsilon_A^b / \lambda_B \epsilon_B^b$. To remove the lumber we write

$$\lambda_A \eta_{AA}^{\frac{1}{2}} \epsilon_A^a / \lambda_B \eta_{BB}^{\frac{1}{2}} \epsilon_B^a = p, \quad \lambda_B \eta_{BB}^{\frac{1}{2}} \epsilon_B^b / \lambda_A \eta_{AA}^{\frac{1}{2}} \epsilon_A^b = q, \qquad (1322, 1)$$

$$\eta_{AA}^{\frac{1}{2}} \eta_{BB}^{\frac{1}{2}} / \eta_{AB} = e^{(\chi_{AA}+\chi_{AB}-2\chi_{AB})/zkT} = e^{-w/zkT}, \qquad (1322, 2)$$

so that the definition of $w$ agrees with its previous definition by formula (1314, 7). Then equations (1321, 14), (1321, 15) and (1321, 17) become respectively

$$x_A + x_A s = \frac{p(x_A - x_A s)}{p + e^{w/zkT}} + \frac{pe^{w/zkT}(x_B + x_A s)}{pe^{w/zkT} + 1}, \qquad (1322, 3)$$

$$x_B + x_A s = \frac{qe^{w/zkT}(x_A + x_A s)}{qe^{w/zkT} + 1} + \frac{q(x_B - x_A s)}{q + e^{w/zkT}}, \qquad (1322, 4)$$

$$\frac{(x_A - x_A s)(x_B - x_A s)}{(x_A + x_A s)(x_B + x_A s)} = \left\{ \frac{(p + e^{w/zkT})(q + e^{w/zkT})}{(pe^{w/zkT} + 1)(qe^{w/zkT} + 1)} \right\}^z. \qquad (1322, 5)$$

Equations (1321, 19) and (1321, 20) for $\overline{n_{AB}}$ become respectively

$$\frac{\overline{n_{AB}}}{\frac{1}{2}zN^l} = (x_A + x_A s)\frac{qe^{w/zkT}}{qe^{w/zkT} + 1} + (x_B - x_A s)\frac{e^{w/zkT}}{q + e^{w/zkT}}, \qquad (1322, 6)$$

$$\frac{\overline{n_{AB}}}{\frac{1}{2}zN^l} = (x_A - x_A s)\frac{e^{w/zkT}}{p + e^{w/zkT}} + (x_B + x_A s)\frac{pe^{w/zkT}}{pe^{w/zkT} + 1}. \qquad (1322, 7)$$

By use of equations (4) and (3) respectively these may be simplified at once to

$$\frac{\overline{n_{AB}}}{\frac{1}{2}zN^l} = \frac{2x_B e^{w/zkT} + 2x_A sq}{q + e^{w/zkT}}, \qquad (1322, 8)$$

$$\frac{n_{AB}}{\frac{1}{2}zN^l} = \frac{2x_A e^{w/zkT} + 2x_A sp}{p + e^{w/zkT}}. \qquad (1322, 9)$$

We have worked through the construction of Bethe's equations in this detail for an $ab$ lattice and the general case $x_A \neq x_B$, because it seems to be at least difficult to appreciate exactly what the method is, unless it is first discussed in this admittedly clumsy way without short cuts. Having arrived at these formulae, which contain only the parameters $p$ and $q$ and the combination of interaction energies $w$, we see that we can in practice obtain correct results by replacing $\epsilon_A^a$, $\epsilon_B^b$ by unity, and putting any two of $\eta_{AA}$, $\eta_{BB}$,

$\eta_{AB}$ equal to unity. This last simplification merely means a suitable change of energy zeros. We need not even retain both $\lambda_A$ and $\lambda_B$, though little would be gained by the loss of symmetry resulting in omitting one of them. In the symmetrical case $x_A = x_B = \frac{1}{2}$, one may even omit both $\lambda$'s.

The reduction of these general equations can be carried still further by the elimination of $p$ or $q$. Equations (3) and (4) can be solved for $x_A s$ giving

$$x_A s e^{-w/zkT} = \frac{x_B p(p+e^{w/zkT}) - x_A(1+pe^{w/zkT})}{p^2 e^{w/zkT} + 2p + e^{w/zkT}}$$

$$= \frac{x_A q(q+e^{w/zkT}) - x_B(1+qe^{w/zkT})}{q^2 e^{w/zkT} + 2q + e^{w/zkT}}. \qquad (1322, 10)$$

The equality of the last pair of expressions yields a quadratic equation for $q$ in terms of $p$, $x_A$, $x_B$ and $e^{w/zkT}$, which factorizes. One factor gives an essentially negative value of $q$, and can be discarded. The other factor gives

$$q = \frac{p + (x_B - x_A)(p + e^{w/zkT})}{1 - (x_B - x_A)(1 + pe^{w/zkT})}. \qquad (1322, 11)$$

We may deduce from this that

$$\frac{q + e^{w/zkT}}{1 + qe^{w/zkT}} = \frac{p + e^{w/zkT} - (x_B - x_A)p(e^{2w/zkT} - 1)}{1 + pe^{w/zkT} + (x_B - x_A)(e^{2w/zkT} - 1)}. \qquad (1322, 12)$$

We may therefore reduce equations (3)–(5) to equation (3) together with

$$\frac{(x_A - x_A s)(x_B - x_A s)}{(x_A + x_A s)(x_B + x_A s)} = \left[\frac{p + e^{w/zkT}}{1 + pe^{w/zkT}} \frac{p + e^{w/zkT} - (x_B - x_A)p(e^{2w/zkT} - 1)}{1 + pe^{w/zkT} + (x_B - x_A)(e^{2w/zkT} - 1)}\right]^z. \qquad (1322, 13)$$

Finally the expressions for $\overline{n_{AB}}$ may be simplified and proved identical by expressing $s$ in (8) in terms of $q$, and $s$ in (9) in terms of $p$. We thus obtain

$$\frac{\overline{n_{AB}}}{\frac{1}{2}zN^l} = 2e^{w/zkT} \frac{x_B p^2 + x_A}{p^2 e^{w/zkT} + 2p + e^{w/zkT}} = 2e^{w/zkT} \frac{x_A q^2 + x_B}{q^2 e^{w/zkT} + 2q + e^{w/zkT}}. \qquad (1322, 14)$$

The equality of the $p$ and $q$ forms in (14) is a direct consequence of (11). The first of equations (10) and (14) together with (13) constitute the complete set of equations of Bethe's first approximation for an $ab$ lattice for any values of the atomic ratios. In their reduced form the essential equations may be written*

$$x_A s = \tfrac{1}{2} e^{w/zkT} \frac{p^2 - 1 + (x_B - x_A)(p^2 + 2pe^{w/zkT} + 1)}{p^2 e^{w/zkT} + 2p + e^{w/zkT}}, \qquad (1322, 15)$$

* Chang, *Proc. Camb. Phil. Soc.* **34**, 224 (1938).

$$\left[\frac{1+pe^{w/zkT}}{p+e^{w/zkT}}\,\frac{1+pe^{w/zkT}+(x_B-x_A)(e^{2w/zkT}-1)}{p+e^{w/zkT}-(x_B-x_A)p(e^{2w/zkT}-1)}\right]^{z-1}$$

$$\times\frac{1}{p}\,\frac{1-(x_B-x_A)(1+pe^{w/zkT})}{p+(x_B-x_A)(p+e^{w/zkT})}=1, \quad (1322, 16)$$

$$\frac{\overline{n_{AB}}}{\frac{1}{2}zN^l}=e^{w/zkT}\,\frac{p^2+1+(x_B-x_A)(p^2-1)}{p^2e^{w/zkT}+2p+e^{w/zkT}}. \quad (1322, 17)$$

When $x_A=x_B=\frac{1}{2}$, these equations reduce to the equations

$$s=\frac{e^{w/zkT}(p^2-1)}{p^2e^{w/zkT}+2p+e^{w/zkT}}, \quad (1322, 18)$$

$$\frac{n_{AB}}{\frac{1}{2}zN^l}=e^{w/zkT}\,\frac{p^2+1}{p^2e^{w/zkT}+2p+e^{w/zkT}}, \quad (1322, 19)$$

where $p$ is a parameter given by the proper root of the equation

$$p=\left(\frac{pe^{w/zkT}+1}{p+e^{w/zkT}}\right)^{z-1} \quad (1322, 20)$$

It is unnecessary for us to develop the consequences of these equations any further, since we shall show in the next section that Bethe's equations are completely equivalent to the equations derived from the assumption of quasi-chemical equilibrium, and we have already studied the consequence of these equations in sufficient detail. We have, however, included this rather elaborate development of the underlying equations of Bethe's method in this detail, because the method has been much discussed, not always in a form which is evidently complete, and it may be helpful to the study of these applications to have all the fundamental equations available in a complete form.

**§ 1323. The equivalence of the equations of Bethe and of the quasi-chemical method. The combinatory formulae of Chang.** We shall now show directly that the method of Bethe described in the last two sections and the quasi-chemical method described in § 1317 are completely equivalent. In applying the quasi-chemical method we used the equation (1317, 12), which we repeat

$$\frac{[A \text{ on } a;\ B \text{ on } b]\,[B \text{ on } a;\ A \text{ on } b]}{[A \text{ on } a;\ A \text{ on } b]\,[B \text{ on } a;\ B \text{ on } b]}=e^{2w/zkT}, \quad (1323, 1)$$

where each [ ] denotes the number of pairs of neighbouring sites occupied in the manner indicated inside the brackets. Equation (1) can be regarded either as itself the basic assumption of the quasi-chemical method, or as derived from an assumed prior combinatory formula (1317, 5). In either

case the whole of the equations of the equilibrium state given in § 1317 may be derived from equation (1).

We can now see that Bethe's method leads at once to formula (1) and therefore to equilibrium results which are identical with those of the quasi-chemical method. The complete set of configurations for a central point $a$ and its $z$ neighbours $b$ leads in Bethe's method to the partition function (1321, 6). If we consider a pair of sites consisting of the central $a$ and some one of its $z$ neighbours $b$, then the four different modes of occupation of this pair contribute to $\Gamma^a$ the following sets of terms respectively:

$$\begin{aligned}
&A \text{ on } a,\ B \text{ on } b: && \lambda_A\lambda_B\eta_{AB}\epsilon_B^b(\lambda_A\eta_{AA}\epsilon_A^b+\lambda_B\eta_{AB}\epsilon_B^b)^{z-1},\\
&B \text{ on } a,\ A \text{ on } b: && \lambda_B\lambda_A\eta_{AB}\epsilon_A^b(\lambda_A\eta_{AB}\epsilon_A^b+\lambda_B\lambda_{BB}\epsilon_B^b)^{z-1},\\
&A \text{ on } a,\ A \text{ on } b: && \lambda_A\lambda_A\eta_{AA}\epsilon_A^b(\lambda_A\eta_{AA}\epsilon_A^b+\lambda_B\eta_{AB}\epsilon_B^b)^{z-1},\\
&B \text{ on } a,\ B \text{ on } b: && \lambda_B\lambda_B\eta_{BB}\epsilon_B^b(\lambda_A\eta_{AB}\epsilon_A^b+\lambda_B\eta_{BB}\epsilon_B^b)^{z-1}.
\end{aligned}$$

But the essential meaning of the terms in the grand partition function is that they express the equilibrium values of the relative frequencies of the corresponding states (configurations). Therefore

$$\frac{[A \text{ on } a;\ B \text{ on } b]\,[B \text{ on } a;\ A \text{ on } b]}{[A \text{ on } a;\ A \text{ on } b]\,[B \text{ on } a;\ B \text{ on } b]} = \frac{\eta_{AB}^2}{\eta_{AA}\eta_{BB}}, \qquad (1323, 2)$$

the remaining factors cancelling. When we use (1322, 2) in (2), we recover (1).

From the method of deriving (2) it is obvious that we could have derived the same result even more briefly by constructing $\Gamma_2$ for a single pair of sites, one $a$ and one $b$, instead of constructing $\Gamma_{z+1}$ for a group of $z+1$ sites. With suitably defined factors $\zeta$, to take account of the interaction of the atom on each site of the pair with all the other sites, we should have

$$\begin{aligned}
&A \text{ on } a,\ B \text{ on } b: && \lambda_A\zeta_A^a\lambda_B\zeta_B^b\eta_{AB},\\
&B \text{ on } a,\ A \text{ on } b: && \lambda_B\zeta_B^a\lambda_A\zeta_A^b\eta_{AB},\\
&A \text{ on } a,\ A \text{ on } b: && \lambda_A\zeta_A^a\lambda_A\zeta_A^b\eta_{AA},\\
&B \text{ on } a,\ B \text{ on } b: && \lambda_B\zeta_B^a\lambda_B\zeta_B^b\eta_{BB},
\end{aligned}$$

from which equation (2) follows immediately. The significant feature of these derivations is that it is not necessary to evaluate the $\epsilon$'s or $\zeta$'s as the case may be, since these quantities are automatically eliminated. This point has already been made clear for regular assemblies without long-range order in Chapter VI. Further the value of $z$ comes in only through the relation between the total number of pairs of neighbours and the number of lattice points. If we define $u$ by $u = w/zkT$ and denote the total number of pairs of neighbours by $n_p$, then $\overline{n_{AB}}/n_p$ is a function of $x_A$ and $u$, and so depends on $z$ only through $u$. On the other hand $\overline{n_{AB}}/N$ is $z$ times a function

of $u$, and consequently the configurational energy per atom is $w$ times a function of $w/z$. Since the whole equilibrium state may be deduced from (1), the equilibrium state given by Bethe's equations, being internally self-consistent as we have verified, must be identical with that derived more simply by the quasi-chemical method. It is an elegant and easy exercise to establish directly the identity of the formulae (1322, 18–20) embodying Bethe's theory for the symmetrical case $x_A = x_B = \frac{1}{2}$, with the formulae (1317, 18, 29) of the quasi-chemical method. It will be found in particular that

$$p = \frac{1+s}{\alpha - s} e^{w/zkT}. \tag{1323, 3}$$

We leave these derivations as an exercise to the reader. The identity in the general case can also be established in a similar way between the equations (1322, 15–17) of Bethe and those of the quasi-chemical method.

Formula (1), as we saw in § 1317, can be derived from an assumed approximate combinatory formula for the number of pairs of neighbours of various types. This assumption of the combinatory formula (1317, 5) therefore implies all the results of Bethe's assumptions. The complete equivalence of the two assumptions in these forms is established by a recent investigation by Chang,* who has shown that the fundamental equations of Bethe's theory, equations (1322, 15–17) imply (to the same accuracy) a combinatory formula equivalent to (1317, 5). We refer the reader for a proof to Chang's paper. The necessary arguments are sufficiently direct but somewhat tedious.

In conclusion we may emphasize once again that Bethe's method for regular assemblies with or without long-range order has been shown to be completely equivalent to the approximations of the quasi-chemical method for pairs of nearest neighbours, for lattice arrangements of type *ab* in which all the neighbours of *a* sites are *b* sites and *vice versa*, and the atoms $A$ and $B$ are present in any atomic ratio. It is probably best to regard this equivalence of Bethe's method to the approximate but explicit partition function for the whole assembly provided by the quasi-chemical method as the reason for the complete internal self-consistency of Bethe's equations[▲]. Bethe himself has shown in his original paper how his method can be extended to still higher approximations, and has given calculations for a second approximation for $z = 6$. There is no doubt that Bethe's approximations of higher order must ultimately converge in the limit to the true formula for the assembly in question, but there is considerable doubt as to the exact status of, for example, the second approximation. It seems possible that it does not preserve the complete internal self-consistency of the first approxima-

* Chang, *Proc. Roy. Soc.* A, 173, 48 (1939).

▲ See appendix, § A 10.

tion or its complete equivalence to a genuine partition function, properties which the limit of the higher order approximations will ultimately regain. These inconsistencies, however, if they exist, do not prevent the judicious use of the second and higher order approximations. They will, however, prevent them from simplifying in any way comparable to that in which we have simplified the first.

**§ 1324. Configurational free energy in the case of two non-equivalent sub-lattices. (Zeroth approximation.)** We now consider a crystal with $N^l$ lattice-points (sites) of which $r_a N^l$ are of type $a$ and $r_b N^l$ of type $b$, where

$$r_a + r_b = 1, \quad r_a < r_b. \tag{1324, 1}$$

No loss of generality is involved in assuming $r_a$ less than $r_b$. We assume that each $a$ site has $z$ neighbours all $b$ sites, but each $b$ site has $z$ neighbours, of which $zr_a/r_b$ are $a$ sites and $z(r_b - r_a)/r_b$ are $b$ sites.

We shall consider only the case where the number of $A$ atoms is equal to the number of $a$ sites, and the number of $B$ atoms is equal to the number of $b$ sites. Thus in the state of most perfect order all the $a$ sites are occupied by $A$ atoms and all the $b$ sites by $B$ atoms. In the state of complete disorder every point will be on the average similarly occupied by $A$'s and $B$'s in proportion to their numbers, that is in the ratio $r_a : r_b$. Any state of intermediate order can be completely described by a single parameter $s$, which can be chosen so that the number of sites of each type occupied by each kind of atom is a linear function of $s$. If we further choose $s$ so that it has the value 1 for the state of complete order and the value 0 for the state of complete disorder, then for any state of intermediate order we have the situation given in Table 6. The parameter $s$ thus defined is called the degree of order.

TABLE 6

*Number of A and B atoms on a and b sites*

| | |
|---|---|
| $A$ on $a$: $r_a(r_a + r_b s) N^l$; | $B$ on $a$: $r_a r_b (1-s) N^l$; |
| $A$ on $b$: $r_a r_b (1-s) N^l$; | $B$ on $b$: $r_b(r_b + r_a s) N^l$. |

The number $g(s)$ of distinguishable configurations of given $s$ is, according to the table,

$$g(s) = \frac{[r_a N^l]!}{[r_a(r_a + r_b s) N^l]!\,[r_a r_b(1-s) N^l]!}\;\frac{[r_b N^l]!}{[r_a r_b(1-s) N^l]!\,[r_b(r_b + r_a s) N^l]!}. \tag{1324, 2}$$

Using Stirling's theorem we can rewrite this as

$$\begin{aligned}\log g(s)/N^l = {} & r_a \log r_a + r_b \log r_b - r_a(r_a + r_b s)\log[r_a(r_a + r_b s)] \\ & - 2r_a r_b(1-s)\log[r_a r_b(1-s)] - r_b(r_b + r_a s)\log[r_b(r_b + r_a s)].\end{aligned} \tag{1324, 3}$$

We shall confine ourselves to the zeroth approximation used by Bragg and Williams, corresponding exactly to that used in § 1314 and summarized by formula (1314, 1). We have therefore merely to calculate $W_{Av}(s)$ and use this in place of $\overline{\overline{W}}(s)$ in the free energy. Denoting the interaction energies of the several kinds of pairs of neighbouring atoms as before by $-2\chi_{AA}/z$, $-2\chi_{AB}/z$, $-2\chi_{BB}/z$ and the numbers of pairs of neighbours of each kind by $n_{AA}$, $n_{AB}$, $n_{BB}$, we have

$$W_{Av}(s) = -\frac{2}{z}\{(n_{AA})_{Av}\chi_{AA} + (n_{AB})_{Av}\chi_{AB} + (n_{BB})_{Av}\chi_{BB}\}, \qquad (1324, 4)$$

where $(n_{AA})_{Av}$, ... are calculated by taking purely random arrangements of the $A$ and $B$ atoms on each pair of neighbouring sites, so long as the given value of $s$ is preserved.

We now calculate $(n_{AA})_{Av}$. We note that $AA$ pairs arise in two ways: (i) when the first $A$ is on an $a$ site and the second on a $b$ site; (ii) when both $A$'s are on $b$ sites. By Table 6 there are on the average $r_a(r_a + r_b s) N^l$ sites $a$ occupied by $A$'s. Each has $z$ neighbours ($b$ sites) of which the average number occupied by $A$'s is $zr_a(1-s)$. This type of $AA$ pair therefore contributes to $(n_{AA})_{Av}$

$$zN^l r_a^2(1-s)(r_a + r_b s)$$

pairs. Again there are on the average $r_a r_b(1-s) N^l$ sites $b$ occupied by $A$'s. Each of these has $z(r_b - r_a)/r_b$ sites $b$ as neighbours and the average fraction of any $b$ sites occupied by $A$'s is, by Table 6, $r_a(1-s)$. Since both $A$ atoms of the pair are on similar sites, we should in this way count such $AA$ pairs twice over, and we must divide by 2. These pairs therefore contribute to $(n_{AA})_{Av}$

$$\tfrac{1}{2}zN^l r_a^2(r_b - r_a)(1-s)^2$$

pairs, and we find

$$\begin{aligned}(n_{AA})_{Av} &= \tfrac{1}{2}zN^l\{r_a^2(r_b - r_a)(1-s)^2 + 2r_a^2(1-s)(r_a + r_b s)\} \\ &= \tfrac{1}{2}zN^l r_a^2(1-s^2). \qquad (1324, 5)\end{aligned}$$

By similar counting we find

$$\begin{aligned}(n_{BB})_{Av} &= \tfrac{1}{2}zN^l\{(r_b - r_a)(r_b + r_a s)^2 + 2r_b r_a(1-s)(r_b + r_a s)\} \\ &= \tfrac{1}{2}zN^l(r_b^2 - r_a^2 s^2); \qquad (1324, 6)\end{aligned}$$

$$\begin{aligned}(n_{AB})_{Av} &= \tfrac{1}{2}zN^l - (n_{AA})_{Av} - (n_{BB})_{Av} \\ &= \tfrac{1}{2}zN^l(2r_a r_b + 2r_a^2 s^2). \qquad (1324, 7)\end{aligned}$$

Substituting from (5), (6), (7) into (4), we obtain

$$W_{Av}(s) = -N^l\{r_a^2\chi_{AA} + 2r_a r_b\chi_{AB} + r_b^2\chi_{BB}\} - N^l r_a^2 s^2\{-\chi_{AA} + 2\chi_{AB} - \chi_{BB}\}. \qquad (1324, 8)$$

If we define a characteristic energy (of unmixing) $w$ by

$$w = -\chi_{AA} + 2\chi_{AB} - \chi_{BB}, \tag{1324, 9}$$

we can write (8) as
$$W_{Av}(s) - W_{Av}(0) = -N^l r_a^2 s^2 w \tag{1324, 10}$$

or as
$$W_{Av}(s) - W_{Av}(1) = N^l r_a^2 (1-s^2) w. \tag{1324, 11}$$

Using $W_{Av}(s)$ given by (10) for $\overline{\overline{W}}(s)$ and formula (3) for $\log g(s)$, we obtain for the configurational free energy

$$\frac{F(s)-F(0)}{N^l kT} = r_a(r_a + r_b s)\log[r_a(r_a + r_b s)] + 2r_a r_b(1-s)\log[r_a r_b(1-s)] + r_b(r_b + r_a s)\log[r_b(r_b + r_a s)] - 2r_a \log r_a - 2r_b \log r_b - r_a^2 s^2 w/kT. \tag{1324, 12}$$

From this formula for $F(s)$ we can derive all the equilibrium properties to the approximation of ignoring the differences between $\overline{\overline{W}}(s)$, $\overline{W}(s)$ and $W_{Av}(s)$.

**§ 1325. Equilibrium properties for the case $r_a = \frac{1}{4}$, $r_b = \frac{3}{4}$.** In studying the consequences of formula (1324, 12) we shall confine ourselves almost entirely to the case $r_a = \frac{1}{4}$, $r_b = \frac{3}{4}$, as this corresponds to the example $Cu_3Au$. When these values of $r_a$, $r_b$ are substituted into (1324, 12), we obtain

$$\{F(s)-F(0)\}/N^l kT = \tfrac{1}{16}\{(1+3s)\log(1+3s) + 6(1-s)\log(1-s) + (9+3s)\log(1+\tfrac{1}{3}s) - s^2 w/kT\}. \tag{1325, 1}$$

The dependence of $F(s)$ on $s$ according to (1) is shown for various temperatures in Fig. 11 and is quite different from the case $r_a = r_b = \frac{1}{2}$ represented in Fig. 5.

At high temperatures the only stationary value of $F(s)$ is a minimum at $s = 0$ and the stable state is that of complete disorder. As the temperature is lowered we reach a range of temperatures in which there is a second minimum say at $s = s^*$; between the two minima there must be a maximum, say at $s = s^\dagger$. The highest temperature $T_1$ at which this occurs is determined by the conditions

$$s^* = s^\dagger = s_1 \neq 0, \quad \partial F/\partial s = 0, \quad \partial^2 F/\partial s^2 = 0. \tag{1325, 2}$$

The state $s = s^\dagger$ is unstable and of no physical interest. The states $s = 0$ and $s = s^*$ are, however, both stable relative to states of infinitesimally different order. But only the state corresponding to the lower minimum will be absolutely stable, the other state being metastable. At higher temperatures the state $s = 0$ is the absolutely stable, at lower temperatures the state $s = s^*$. The transition temperature $T_t$ at which the two minima are equal is determined by the conditions

$$s = s^* = s_t, \quad \partial F/\partial s = 0, \quad F(s) - F(0) = 0. \tag{1325, 3}$$

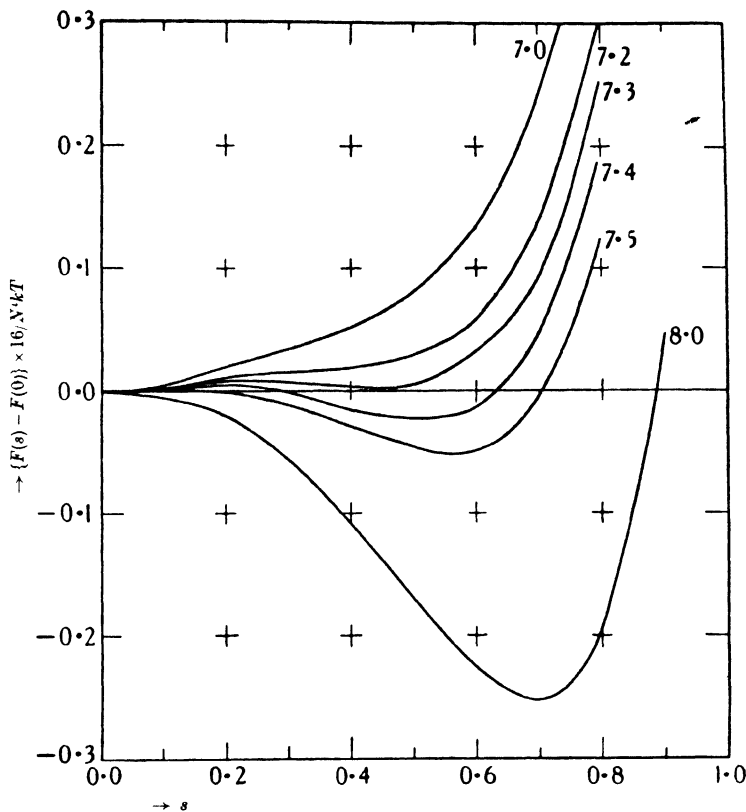



Fig. 11. Dependence of the configurational free energy $F(s)$ on the degree of order $s$ for $AB_3$ according to the zeroth (B.-W.) approximation for various temperatures. The numbers attached to the curves are values of $w/kT$

At still lower temperatures $s = s^*$ is the only minimum, the state $s = 0$ having become a maximum. The temperature $T_2$ at which $s_0 = 0$ changes from a minimum to a maximum is determined by the conditions

$$s = s^\dagger = 0, \quad \partial F/\partial s = 0, \quad \partial^2 F/\partial s^2 = 0. \tag{1325, 4}$$

Differentiating formula (1) with respect to $s$, we obtain

$$\frac{\partial F/\partial s}{N'kT} = \frac{1}{16}\left\{3 \log \frac{(1+3s)(1+\frac{1}{3}s)}{(1-s)^2} - 2s\frac{w}{kT}\right\}, \tag{1325, 5}$$

and the condition $\partial F/\partial s = 0$ is therefore equivalent to

$$\frac{w}{kT} = \frac{3}{2}\log\left\{1 + \frac{16s}{3(1-s)^2}\right\} \tag{1325, 6}$$

This relation between $s$ and $T$ is shown in Fig. 12. Differentiating (5) with respect to $s$, we obtain

$$\frac{\partial^2 F/\partial s^2}{N^l kT} = \frac{1}{16}\left\{\frac{9}{1+3s}+\frac{1}{1+\frac{1}{3}s}+\frac{6}{1-s}-2\frac{w}{kT}\right\}. \qquad (1325,7)$$

Using (6) and (7) in (2), we find that $T_1$ is given by

$$\frac{w}{kT_1} = \frac{3}{2s_1}\log\left\{1+\frac{16s_1}{3(1-s_1)^2}\right\} = \frac{4\frac{1}{2}}{1+3s_1}+\frac{\frac{1}{2}}{1+\frac{1}{3}s_1}+\frac{3}{1-s_1}. \quad (1325,8)$$

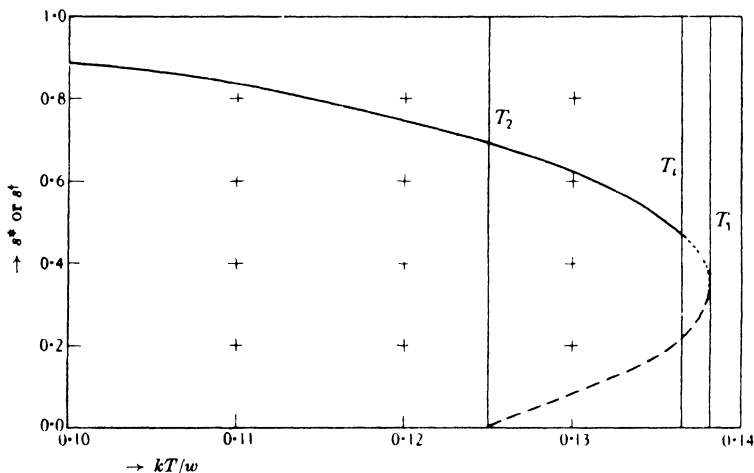



Fig. 12. Dependence on temperature, according to zeroth (B.-W.) approximation, of the value $s^*$ of $s$ which minimizes $F(s)$ and of the value $s^†$ of $s$ which maximizes $F(s)$.
—— Stable; lowest minimum. ······ Metastable; minimum but not lowest. ------ Unstable; maximum.

Solving this numerically we obtain $s_1 = 0{\cdot}345$ and $w/kT_1 = 7{\cdot}24$ or $kT_1 = 0{\cdot}138w$. Using (1) and (5) in (3), we find that $T_t$ is given by

$$\frac{w}{kT_t} = \frac{1}{s_t^2}\{(1+3s_t)\log(1+3s_t)+6(1-s_t)\log(1-s_t)+(9+3s_t)\log(1+\tfrac{1}{3}s_t)\}$$
$$= \frac{3}{2s_t}\log\frac{(1+3s_t)(1+\frac{1}{3}s_t)}{(1-s_t)^2} \qquad (1325,9)$$

The second of these equations can be written in the shorter form

$$(1+\tfrac{3}{2}s_t)\log(1+3s_t)+(6-3s_t)\log(1-s_t)+(9+\tfrac{3}{2}s_t)\log(1+\tfrac{1}{3}s_t) = 0. \qquad (1325,10)$$

Solving this numerically we find* $s_t = 0{\cdot}463$, and substituting this back into (9) we find $w/kT_t = 7{\cdot}32$ or $kT_t = 0{\cdot}137w$. Using (7) in (4) we find

* The value 0·467 given in *S.M.* is not quite accurate.

$w/kT_2 = 8$ or $kT_2 = 0{\cdot}125w$. The three temperatures $T_1$, $T_t$, and $T_2$ are shown in Fig. 12.

The configurational energy $E(s)$ is given by

$$\{E(s) - E(1)\}/N^l = r_a^2(1-s^2)\,w = \tfrac{1}{16}(1-s^2)\,w \qquad (1325, 11)$$

for $r_a = \frac{1}{4}$, $r_b = \frac{3}{4}$, and its equilibrium value at any temperature $T \leqslant T_t$ is obtained by substituting into (11) the equilibrium value $s^*$ of $s$ determined by (6). This dependence of $E(s)$ on $T/T_t$ is shown in Fig. 13. The atomic

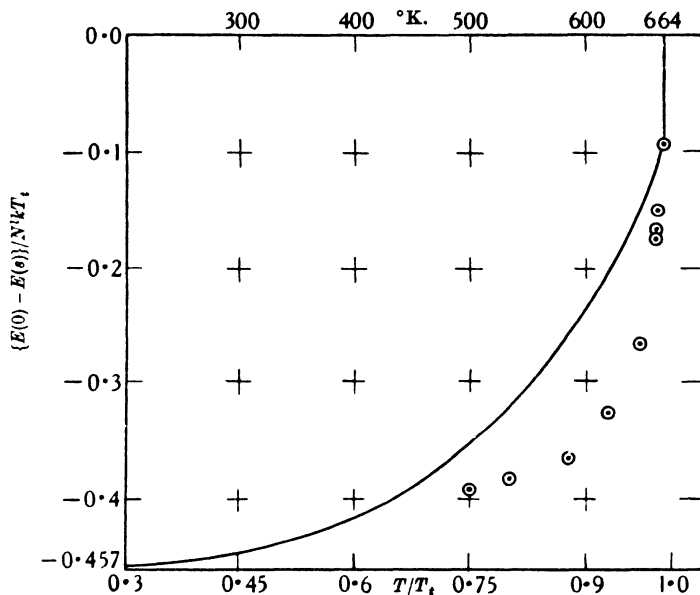



Fig. 13. Dependence on temperature of configurational energy for $Cu_3Au$. ⊙ Experimental data of Sykes and Jones. —— Curve calculated by zeroth (B.-W.) approximation.

energy of transition from the state of order $s_t$ to the state of disorder at the transition temperature $T_t$ is given by

$$\{E(0) - E(s_t)\}/N^l = \tfrac{1}{16}s_t^2 w. \qquad (1325, 12)$$

Using in (12) the numerical values already found for $s_t$ and $T_t$, we obtain†

$$\{E(0) - E(s_t)\}/N^l = 0{\cdot}0134w = 0{\cdot}098kT_t. \qquad (1325, 13)$$

**§ 1326. More accurate treatment of two non-equivalent sub-lattices.** The method described in §§ 1321–1323 has been extended by Peierls‡ to a lattice of the type $Cu_3Au$, taking into account the interactions

† The numerical values given in *S.M.* are not quite accurate.

‡ Peierls, *Proc. Roy. Soc.* A, **154**, 207 (1936). See also Easthope, *Proc. Camb. Phil. Soc.* **33**, 502 (1937).

between all pairs of nearest neighbours in a group consisting of a central site and its nearest neighbours, some of which are nearest neighbours of one other. This application is distinctly laborious and not much use has been made of his results. It is interesting to observe that the quasi-chemical method can also be used for this problem and leads to a pair of independent quadratic equations similar to (1317, 11). Their solutions give the whole of the equilibrium properties of the assembly by simple and direct, if somewhat tedious, calculations. A comparison of these simple formulae with those of Peierls has not yet been made. We must therefore confine ourselves to this statement indicative of the power of the quasi-chemical method, which incidentally shows promise of still wider applications without serious increase of complication.

**§ 1327. Comparison with experimental data for** $Cu_3Au$. We shall now briefly compare the theory with the experimental data for $Cu_3Au$.

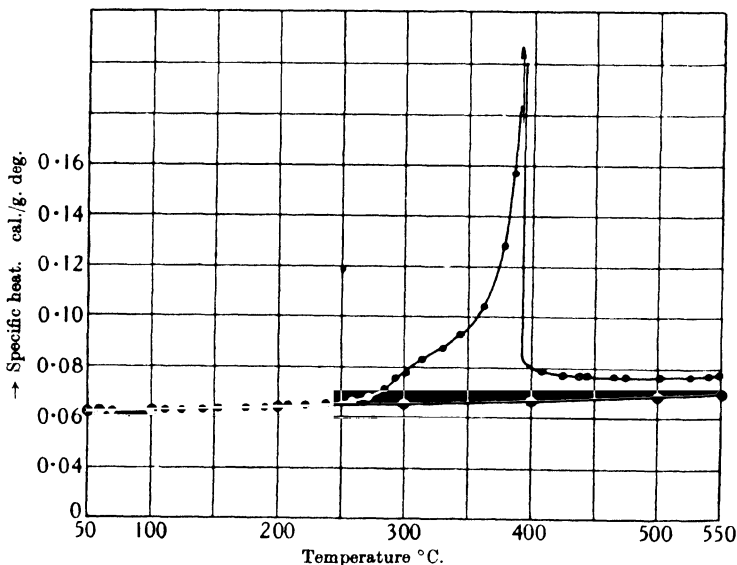



Fig. 14. Specific heat of $Cu_3Au$. Experimental data of Sykes and Jones. The lower curve and points marked ⊕ are calculated from the values for Cu and Au by the simple law for mixtures.

This alloy has been thoroughly investigated by Sykes and Jones.* Their experimental curve for the heat capacity is given in Fig. 14, which clearly shows the transition temperature at 664° K. The experiments of Sykes and

* Sykes and Jones, *Proc. Roy. Soc.* A, **157**, 213 (1936), where references will be found to earlier papers.

Jones confirm the existence of a finite heat of transition, which they find to be $1{\cdot}26 \pm 0{\cdot}13$ cal./g. This corresponds to a value of $\{E(0) - E(s_t)\}/N^l kT$ of $0{\cdot}093 \pm 0{\cdot}009$ as compared with the value 0·098 given by formula (1325, 12) for the B.-W. approximation. This agreement may be fortuitous, since according to Peierls* it disappears when the B.-W. approximation is replaced by a better approximation.

The experimental configurational energy is plotted as a function of temperature in Fig. 13, where the theoretical curve according to the zeroth (B.-W.) approximation is also given.† It is clear that the energy change is considerably more concentrated near the transition temperature than is predicted by the theory. The theoretical curve corresponding to the first approximation (Q.-C. or B.) has not yet been calculated accurately, but according to the calculations by Peierls the agreement between observation and theory is not improved by using the first approximation instead of the zeroth. It appears that the theory does not go deep enough to give more than a semi-quantitative account of the actual behaviour of these alloys and may need radical revision before it can be regarded as a trustworthy quantitative theory.

**§ 1328. Variations of type of order.** In discussing $Cu_3Au$ we defined the degree of order $s$ with respect to the superlattice shown in Fig. 4*c*, which does in fact correspond to the structure of $Cu_3Au$ at low temperatures. The alloy CuAu has an entirely different superlattice structure consisting of alternate layers of Cu and Au. Since then alloys of copper and gold can have at least these two distinct kinds of superlattice, it may reasonably be asked what justification we have for completely ignoring the second kind of superlattice in our discussion of $Cu_3Au$. The answer‡ is that strictly the partition function consists of a sum of terms for all possible degrees of order of all possible kinds, but as usual it is permissible to replace the complete partition function by the dominating term or groups of terms. The justification for considering only the type of superlattice shown in Fig. 4*c* is simply that for alloys having compositions approximating to $Cu_3Au$ the type of order corresponding to this superlattice dominates in the partition function and the terms in the partition function corresponding to order relative to a superlattice of alternate layers are entirely negligible. For compositions

* See Peierls, *Proc. Roy. Soc.* A, **154**, 207 (1936), especially Fig. 3.

† The theoretical curve is given correctly by Bragg and Williams, *Proc. Roy. Soc.* A, **151**, 561 (1935), Fig. 8. Unfortunately the curve given by Sykes and Jones, *Proc. Roy. Soc.* A, **157**, 219 (1936), Fig. 3, curve *b*, is based on Bragg and Williams, *Proc. Roy. Soc.* A, **145**, 711 (1934), Fig 7, which is wrongly drawn. Nix and Shockley, *Rev. Mod. Phys.* **10**, 1 (1938) in Fig. 37, copy the incorrect curve, but give the correct curve in Fig. 12.

‡ See Chang, *Proc. Camb. Phil. Soc.* **35**, 265 (1939).

approximating to CuAu the situation is reversed. There may be, and as a matter of fact there is, an intermediate range of compositions where it is necessary to include both types of terms in the partition function. This range of concentrations and the transitions from one type of order to another have been discussed by Shockley* and by Easthope.† We shall not here give details. We shall only mention that, if one considers the possible occurrence of only one type of order at a time, and constructs the curve for the free energy (or for minus the logarithm of the partition function) against composition for a given temperature, one will obtain two or more intersecting curves with a common tangent below them. The portions of both curves between the two points of contact correspond to metastable states, the stable state for the relevant compositions being a mixture of two phases represented by the points of contact.

Similar considerations apply to the terms in the partition function corresponding to order (of the important kind) and the terms corresponding to the absence of any long-range order. If we know that the temperature in which we are interested is above the order-disorder Curie temperature, we may safely omit the terms corresponding to order and in fact ignore the possibility of order. This is precisely what we did in our treatment of regular solutions in Chapter VIII and regular monolayers in Chapter X.

**§ 1329. Anomalous thermal expansion.** Hitherto we have treated the energy of unmixing $w$ as a constant, whereas in fact we must expect $w$ to change with temperature owing to the thermal expansion of the crystal. We can improve our previous treatment by regarding $w$ as a function of $v = V/N^l$. For the sake of brevity we shall restrict our discussion to the zeroth (B.-W.) approximation and to exact atomic ratios ($x_A = r_a$, $x_B = r_b$). $F$ is then given by

$$\frac{F-F^0}{N^l} = -kT\log\frac{g(s)}{g(0)} - r_a^2 s^2 w(v), \qquad (1329,1)$$

where the superscript zero refers to the value for $s = 0$ and the given values of $T$, $v$. The equilibrium value of $s$ to be inserted into (1) is as usual determined by the condition

$$(\partial F/\partial s)_{T,v} = 0. \qquad (1329,2)$$

We can now obtain the pressure by differentiating (1) with respect to $v$. In virtue of (2) we ignore the variations of $s$ and so obtain simply

$$P-P^0 = r_a^2 s^2 \frac{dw}{dv}. \qquad (1329,3)$$

* Shockley, *J. Chem. Phys.* **6**, 130 (1938).
† Easthope, *Proc. Camb. Phil. Soc.* **34**, 68 (1938).

If we denote the coefficient of thermal expansion by $\alpha$ and the compressibility by $\beta$, we obtain by differentiating (3) with respect to $T$

$$\left(\frac{\partial P}{\partial T}\right)_V - \left(\frac{\partial P^0}{\partial T}\right)_V = \frac{\alpha}{\beta} - \frac{\alpha^0}{\beta^0} = -r_a^2 \frac{w}{kT^2} \frac{ds^2}{d(w/kT)} \frac{dw}{dV}. \qquad (1329, 4)$$

Similarly by differentiating (3) with respect to $V$, we obtain

$$-V\left(\frac{\partial P}{\partial V}\right)_T + V\left(\frac{\partial P^0}{\partial V}\right)_T = \frac{1}{\beta} - \frac{1}{\beta^0} = -Vr_a^2 \left\{\frac{1}{kT} \frac{ds^2}{d(w/kT)} \left(\frac{dw}{dV}\right)^2 + s^2 \frac{d^2w}{dV^2}\right\}. \qquad (1329, 5)$$

By comparing (4) with (5) it can be verified that

$$\left(\frac{1}{\beta} - \frac{1}{\beta^0}\right) \Big/ \left(\frac{\alpha}{\alpha^0 \beta} - \frac{1}{\beta^0}\right) \simeq \alpha^0 T \simeq 10^{-3} \ll 1. \qquad (1329, 6)$$

It is therefore sufficiently accurate to replace (4) by

$$\alpha - \alpha^0 = -\beta^0 r_a^2 \frac{w}{kT^2} \frac{ds^2}{d(w/kT)} \frac{dw}{dV}. \qquad (1329, 7)$$

In the simple case $r_a = r_b = \frac{1}{2}$ we found in § 1315 that formula (2) becomes

$$\frac{w}{2kT} = \frac{1}{s} \operatorname{arc\,tanh} s \quad (0 < T_c - T \ll T_c). \qquad (1329, 8)$$

Immediately below the Curie temperature we have by expansion of (8) in powers of $s$

$$\frac{w}{2kT} = 1 + \tfrac{1}{3}s^2 \quad (0 < T_c - T \ll T_c). \qquad (1329, 9)$$

Using (9) in (7) we obtain

$$\alpha - \alpha^0 = -\beta^0 \frac{3}{2} \frac{w}{kT_c^2} \frac{dw}{dV} \quad (0 < T_c - T \ll T_c). \qquad (1329, 10)$$

Immediately above the Curie temperature $ds/dT = 0$ and consequently

$$\alpha - \alpha^0 = 0 \quad (T > T_c). \qquad (1329, 11)$$

There should therefore be a discontinuity in the coefficient of thermal expansion at the Curie temperature.

When there is a discontinuity in $s$, we see from (3) that, since $P$ must be continuous, either $dw/dV = 0$ or there is a discontinuity in the volume.

Unless $dw/dV$ is zero or negligibly small, we are therefore led to expect a discontinuity in $\alpha$ at the Curie point of CuZn and a discontinuity of volume at the transition point of $Cu_3Au$. Recent measurements by Nix* have revealed a discontinuity of $\alpha$ but not of $V$ in copper-gold alloys. The discrepancy between theory and experiment is at present unexplained.

* Nix and MacNair, *Phys. Rev.* **60**, 320 (1941).

## CHAPTER XIV

### ELECTRIC AND MAGNETIC PROPERTIES

**§ 1400. Introduction.** It may seem ambitious to attempt to deal in one chapter with a subject more suitable for a whole book. It may also seem uncalled for, inasmuch as there are available such excellent books on the subject. In particular we may mention those of Van Vleck* and of Stoner.† Since, however, there is no other field in which the application of statistical mechanics has been more fruitful, we have decided to include an account, even if a meagre one, of this successful application of the theory. We shall try to give a balanced description of the general principles and results, merely giving references to sources of more detailed treatment. Our main sources of information have been the two books referred to above. The subject-matter in §§ 1415–1416 and § 1427 onwards is, however, more recent than the text-books, but here again the most important contributions to the theory are contained in papers by Van Vleck (non-metallic substances) and by Stoner (metals).

**§ 1401. Classical Hamiltonian.** We shall require to know something of the form of Schrödinger's equation for a system in a uniform external electric or magnetic field, but before writing this down it is instructive to consider briefly its classical analogue, namely the Hamiltonian form for the energy and the Hamiltonian equations of motion. The discussion‡ should help to clarify one of the most important differences between the electric and magnetic cases, namely the absence of any electrical analogue of diamagnetism.

Let us first consider a system consisting of particles of mass $m_i$ and charges $e_i$, in a uniform external electric field $E_z$ in the $z$-direction. We use $x_i$, $y_i$, $z_i$ and $p_{x_i}$, $p_{y_i}$, $p_{z_i}$ to denote the cartesian coordinates and conjugate momenta of the particle $i$. Then the Hamiltonian $\mathscr{H}$ is

$$\mathscr{H} = \Sigma_i \tfrac{1}{2}(p_{x_i}^2 + p_{y_i}^2 + p_{z_i}^2)/m + U(x_1, y_1, z_1, \ldots) - E_z \Sigma_i e_i z_i, \quad (1401, 1)$$

where $U$ denotes the mutual electrostatic energy of the particles. We might expect another term for the mutual electromagnetic energy of the particles; strictly there is such a term but it is small of the order $(\dot{x}/c)^2$, where $c$ denotes the velocity of light, and there would be no sense in including a term of this

* Van Vleck, *Electric and Magnetic Susceptibilities* (Oxford, 1932). Hereafter referred to merely as Van Vleck.

† Stoner, *Magnetism and Matter* (Methuen, 1934). Hereafter referred to merely as Stoner.

‡ The discussion which follows is a brief résumé of Van Vleck, pp. 19–22.

order, as long as we are ignoring relativity corrections of the same order. The Hamiltonian equations of motion for the $z$-direction are

$$\dot{z}_i = \frac{\partial \mathscr{H}}{\partial p_{z_i}} = \frac{p_{zi}}{m_i}, \tag{1401, 2}$$

$$\dot{p}_{z_i} = -\frac{\partial \mathscr{H}}{\partial z_i} = -\frac{\partial U}{\partial z_i} + e_i E_z. \tag{1401, 3}$$

From (2) we can verify that the momentum $p_{z_i}$ is simply the product of the mass $m_i$ and the velocity $\dot{z}_i$, just as in the absence of the field. From (3) we can verify that the presence of the field $E_z$ is equivalent to a force $e_i E_z$ in the $z$-direction. This confirms the correctness of the form (1) assumed for the Hamiltonian. The electric moment of the system has a $z$-component $\mu_z$, which can be defined by

$$\mu_z = \Sigma_i e_i z_i, \tag{1401, 4}$$

or alternatively by

$$\mu_z = -\partial \mathscr{H}/\partial E_z. \tag{1401, 5}$$

There is nothing particularly striking in any of the above relations until we compare them with their magnetic analogues.

Let us now consider the same system of particles in a uniform external magnetic field $H_z$ in the $z$-direction. Using right-handed axes, the Hamiltonian is now

$$\mathscr{H} = \Sigma_i \frac{p_{x_i}^2 + p_{y_i}^2 + p_{z_i}^2}{2m_i} + U(x_1, y_1, z_1, \ldots) - H_z \Sigma_i \frac{e_i}{c} \frac{1}{2m_i}(x_i p_{y_i} - y_i p_{x_i}) + H_z^2 \Sigma_i \frac{e_i^2}{8m_i c^2}(x_i^2 + y_i^2). \tag{1401, 6}$$

The Hamiltonian equations of motion for the $x$- and $y$-directions are

$$\dot{x}_i = \frac{\partial \mathscr{H}}{\partial p_{x_i}} = \frac{p_{xi}}{m_i} + \frac{e_i}{c}\frac{1}{2m_i} H_z y_i, \tag{1401, 7}$$

$$\dot{y}_i = \frac{\partial \mathscr{H}}{\partial p_{y_i}} = \frac{p_{yi}}{m_i} - \frac{e_i}{c}\frac{1}{2m_i} H_z x_i, \tag{1401, 8}$$

$$\dot{p}_{x_i} = -\frac{\partial \mathscr{H}}{\partial x_i} = -\frac{\partial U}{\partial x_i} + \frac{e_i}{c}\frac{1}{2m_i} H_z p_{y_i} - \frac{H_z^2 e_i^2}{4m_i c^2} x_i, \tag{1401, 9}$$

$$\dot{p}_{y_i} = -\frac{\partial \mathscr{H}}{\partial y_i} = -\frac{\partial U}{\partial y_i} - \frac{e_i}{c}\frac{1}{2m_i} H_z p_{x_i} - \frac{H_z^2 e_i^2}{4m_i c^2} y_i. \tag{1401, 10}$$

If we differentiate (7) with respect to the time and substitute for $\dot{p}_{x_i}$ from (9), we obtain

$$m_i \ddot{x}_i = -\frac{\partial U}{\partial x_i} + \frac{e_i}{cm_i} H_z p_{y_i} - \frac{H_z^2 e_i^2}{2m_i c^2} x_i. \tag{1401, 11}$$

If we now eliminate $p_y$ from (8) and (11), we obtain

$$m_i \ddot{x}_i = -\frac{\partial U}{\partial x_i} + \frac{e_i \dot{y}_i}{c} H_z. \tag{1401, 12}$$

By an exactly similar procedure we can obtain

$$m_i \ddot{y}_i = -\frac{\partial U}{\partial y_i} - \frac{e_i \dot{x}_i}{c} H_z. \qquad (1401, 13)$$

Formulae (12) and (13) express the familiar fact that the presence of the magnetic field $H_z$ is equivalent to a force $H_z e_i \dot{y}_i/c$ in the $x$-direction and a force $-H_z e_i \dot{x}_i/c$ in the $y$-direction. This verifies the correctness of the form (6) assumed for the Hamiltonian. It is important to observe that the momenta $p_{x_i}$, $p_{y_i}$ are not equal to $m_i \dot{x}_i$, $m_i \dot{y}_i$ respectively, but are related to them according to (7) and (8). It is this non-vanishing of $p_{x_i} - m_i \dot{x}_i$ and $p_{y_i} - m_i \dot{y}_i$ which necessitates the presence of the terms in $H_z^2$ in the Hamiltonian. We shall see shortly that these terms, which have no electrical analogue, lead to diamagnetism. We shall provisionally define the magnetic moment to be a vector whose $z$-component* $\mu_z$ is given by

$$\mu_z = -\partial \mathscr{H}/\partial H_z. \qquad (1401, 14)$$

This is the magnetic analogue of (5) and we shall verify that it agrees with the familiar conception of a magnetic moment. Substituting from (6) into (14), we obtain

$$\mu_z = \Sigma_i \frac{e_i}{2m_i c}(x_i p_{y_i} - y_i p_{x_i}) - H_z \Sigma_i \frac{e_i^2}{4m_i c^2}(x_i^2 + y_i^2). \qquad (1401, 15)$$

If we substitute for $p_{x_i}$ and $p_{y_i}$ from (7) and (8) into (15), we obtain

$$\mu_z = \Sigma_i \frac{e_i}{2c}(x_i \dot{y}_i - y_i \dot{x}_i) = \Sigma_i \frac{e_i}{2m_i c} M_{z_i}, \qquad (1401, 16)$$

where $M_{z_i}$ denotes the angular momentum about the $z$-axis. Formula (16) expresses the well-known equivalence between a magnet and a charge circulating about the axis of the magnet. This verifies the correctness of the assumed definition (14) of $\mu_z$.

The form (16) for $\mu_z$ is certainly more familiar than the form (15), being more closely related to Ampère's elementary currents. It is, however, the form (15) rather than (16) which has a quantal analogue, because it expresses $\mu_z$ as a function of the canonical variables $x_i$, $p_{x_i}$ and $y_i$, $p_{y_i}$. It is of fundamental importance that when $\mu_z$ is expressed in terms of the canonical variables it contains terms of first order in the field $H_z$ as well as terms of zero order. The first order terms are called the *diamagnetic* terms and the zero order the *paramagnetic*.

**§ 1402. Schrödinger's equation.** Schrödinger's equation is constructed by analogy with the Hamiltonian. For a system in an external

* We use the same symbol $\mu$ for an electric and a magnetic moment. It will always be obvious which is being referred to.

electric field $E_z$ in the $z$-direction we have as the quantal analogue of (1401, 1)

$$\left\{\Sigma_i - \frac{h^2}{8\pi^2 m_i}\left(\frac{\partial^2}{\partial x_i^2}+\frac{\partial^2}{\partial y_i^2}+\frac{\partial^2}{\partial z_i^2}\right)+U(x_1, y_1, z_1, \ldots)-E_z\Sigma_i e_i z_i-\epsilon\right\}\psi = 0. \tag{1402, 1}$$

In principle at least we can suppose solutions obtained of the form

$$\epsilon = \epsilon^0 + aE_z + \tfrac{1}{2}bE_z^2, \tag{1402, 2}$$

where $\epsilon^0$ denotes an energy level for zero field. The particular terms in $E_z$ and $E_z^2$ are referred to respectively as *the linear and quadratic Stark effects*. Higher order terms are negligible at ordinary field strengths. Generally the field will remove degeneracy, so that a degenerate energy level $\epsilon^0$ is split by the field into several levels $\epsilon$ with different values of the parameters $a$ and $b$. When the system is in a specified state with given $\epsilon^0$, $a$, $b$, its electric moment in the $z$-direction is

$$\mu_z = -\partial\epsilon/\partial E_z = -(a+bE_z). \tag{1402, 3}$$

The statistical problem is to find the average moment $\bar{\mu}_z$ over all states or energy levels of the system.

For a system in a magnetic field Schrödinger's equation constructed by analogy with (1401, 6) is

$$\left\{\Sigma_i - \frac{h^2}{8\pi^2 m_i}\left(\frac{\partial^2}{\partial x_i^2}+\frac{\partial^2}{\partial y_i^2}+\frac{\partial^2}{\partial z_i^2}\right)+U(x_1, y_1, z_1, \ldots)-H_z\Sigma_i\frac{e_i h}{4\pi i m_i c}\left(x_i\frac{\partial}{\partial y_i}-y_i\frac{\partial}{\partial x_i}\right)\right.$$
$$\left.+H_z^2\Sigma_i\frac{e_i^2}{8m_i c^2}(x_i^2+y_i^2)-\epsilon\right\}\psi = 0. \tag{1402, 4}$$

Solutions can, at least in principle, be obtained in the form

$$\epsilon = \epsilon^0 + aH_z + \tfrac{1}{2}b_{(p)}H_z^2 + \tfrac{1}{2}b_{(d)}H_z^2, \tag{1402, 5}$$

terms of higher order in $H_z$ being negligible at ordinary field strengths. The terms in $H_z$ and $H_z^2$ are referred to as *the linear and quadratic Zeeman effects* respectively. We have written the quadratic effect as two terms with coefficients $b_{(p)}$ and $b_{(d)}$, the former representing the second order perturbation due to the term in $H_z$ in Schrödinger's equation (the first order perturbation yielding the term $aH_z$), and the latter representing the first order perturbation due to the term in $H_z^2$ in Schrödinger's equation (the second order perturbation being of the order $H_z^4$ and so negligible). Generally the field will split a degenerate energy level $\epsilon^0$ into several levels $\epsilon$ with different values of the coefficients $a$, $b_{(p)}$, $b_{(d)}$. When the system is in a specified state with given $\epsilon^0$, $a$, $b$, its magnetic moment in the $z$-direction is

$$\mu_z = -\partial\epsilon/\partial H_z = -(a+b_{(p)}H_z)-b_{(d)}H_z. \tag{1402, 6}$$

The statistical problem is then to determine $\bar{\mu}_z$ the average of $\mu_z$ over all states. When this averaging is carried out it is found that the contribution of the paramagnetic terms $(a+b_{(p)}H_z)$ is always of opposite sign to that of the diamagnetic terms $b_{(d)}H_z$.

**§ 1403. General statistical formulae.** In referring to energy levels we shall use the subscript $j$ to distinguish levels which are separate in the absence of any field, and the subscript $m$ to refer to further separations due to removal of degeneracy by the field. With this notation formula (1402, 2) becomes, when we drop the subscript $z$ for the direction of the field,

$$\epsilon_{j,m} = \epsilon_j^0 + a_{j,m}E + \tfrac{1}{2}b_{j,m}E^2. \qquad (1403, 1)$$

Formula (1402, 5) becomes similarly

$$\epsilon_{j,m} = \epsilon_j^0 + a_{j,m}H + \tfrac{1}{2}b_{(p)j,m}H^2 + \tfrac{1}{2}b_{(d)j,m}H^2. \qquad (1403, 2)$$

If we now construct the partition function $f(T)$,

$$f(T) = \Sigma_j \Sigma_m e^{-\epsilon_{j,m}/kT}, \qquad (1403, 3)$$

the equilibrium number $n_{j,m}$ of systems, out of a total number $N$, which are in the level $\epsilon_{j,m}$ is given by

$$n_{j,m} = N\frac{e^{-\epsilon_{j,m}/kT}}{f(T)} = -NkT\frac{\partial \log f(T)}{\partial \epsilon_{j,m}}. \qquad (1403, 4)$$

But according to (1402, 3) the component of the electric moment parallel to the electric field $E$ in the state $j$, $m$ is

$$\mu_{j,m} = -\partial\epsilon_{j,m}/\partial E. \qquad (1403, 5)$$

From (4) and (5) we deduce for the average moment of the assembly parallel to the field

$$NkT\frac{\partial \log f(T)}{\partial \epsilon_{j,m}}\frac{\partial \epsilon_{j,m}}{\partial E} = NkT\frac{\partial \log f(T)}{\partial E}, \qquad (1403, 6)$$

or for the average moment $\bar{\mu}$ parallel to the field of a single system

$$\bar{\mu} = kT\,\partial \log f(T)/\partial E. \qquad (1403, 7)$$

In just the same way we find for the average magnetic moment parallel to a magnetic field

$$\bar{\mu} = kT\,\partial \log f(T)/\partial H. \qquad (1403, 8)$$

Formulae (7) and (8) are perfectly general and follow from the definition of electric and magnetic moments. We shall now assume that the energy levels are of the forms (1) and (2), and shall neglect terms of higher order than $E^2$ and $H^2$, since in practice these would be negligibly small for ordinary fields. In the electrical case we have

$$f(T) = \Sigma_j e^{-\epsilon_j^0/kT}\Sigma_m\left\{1 - \frac{a_{j,m}E}{kT} + \frac{1}{2}\frac{a_{j,m}^2E^2}{k^2T^2} - \frac{1}{2}\frac{b_{j,m}E^2}{kT}\right\}, \qquad (1403, 9)$$

and so by (7)

$$\bar{\mu} = \Sigma_j e^{-\epsilon_j^0/kT} \Sigma_m \left\{ -a_{j,m} + \frac{a_{j,m}^2 E}{kT} - b_{j,m} E \right\} \Big/ f(T). \quad (1403, 10)$$

We assume that the average moment $\bar{\mu}$ must vanish for zero field. The condition for this is

$$\Sigma_m a_{j,m} = 0 \quad (\text{all } j). \quad (1403, 11)$$

Subject to this condition equation (10) reduces to

$$\bar{\mu} = \Sigma_j e^{-\epsilon_j^0/kT} \Sigma_m \left\{ \frac{a_{j,m}^2 E}{kT} - b_{j,m} E \right\} \Big/ f(T). \quad (1403, 12)$$

At ordinary temperatures there is no sign of saturation even with the strongest available fields, so that $\bar{\mu}$ is proportional to $E$. Under these conditions we can ignore higher powers of $E$ and replace $f(T)$ in the denominator by $\Sigma_j \varpi_j e^{-\epsilon_j^0/kT}$ (we have already rejected higher powers of $E$ in the numerator). We thus find

$$\frac{\bar{\mu}}{E} = \Sigma_j e^{-\epsilon_j^0/kT} \Sigma_m \left\{ \frac{a_{j,m}^2}{kT} - b_{j,m} \right\} \Big/ \Sigma_j \varpi_j e^{-\epsilon_j^0/kT}. \quad (1403, 13)$$

In the magnetic case we obtain by exactly analogous reasoning

$$\frac{\bar{\mu}}{H} = \Sigma_j e^{-\epsilon_j^0/kT} \Sigma_m \left\{ \frac{a_{j,m}^2}{kT} - b_{(p)j,m} - b_{(d)j,m} \right\} \Big/ \Sigma_j \varpi_j e^{-\epsilon_j^0/kT}. \quad (1403, 14)$$

We may call $\bar{\mu}/E$ and $\bar{\mu}/H$ *the electric and magnetic atomic* (*or ionic or molecular*) *susceptibilities* respectively.

All the formulae of this section are based on the assumption that all the systems are completely independent and that there is no appreciable interaction between them. In the electric case this restricts the formulae to gases. The modification of the formulae to apply to liquids is a complicated problem, not yet completely solved, which will be discussed in §§ 1425–1429. In the magnetic case the condition of absence of appreciable interaction is at ordinary temperatures satisfied by all substances other than ferromagnetics. The behaviour of magnetic substances at low temperatures will be discussed in §§ 1431–1436, and ferromagnetism in §§ 1445–1448. Meanwhile we proceed to consider in detail assemblies in which interaction is negligible.

**§ 1404. Electric and magnetic types of molecules.** Up to this point it would appear that the electric case is simpler than the magnetic, owing to the absence of any electric analogue of diamagnetism. When, however, we come to detailed applications, a more or less strict quantal treatment can be applied to magnetic systems, but not to electric ones. The reason is the following. Diamagnetism is practically temperature indepen-

dent and therefore from a thermodynamic point of view rather uninteresting. It is paramagnetism that is highly sensitive to temperature and therefore of the greatest interest from a thermodynamic point of view. We shall find that the great majority of systems showing typical paramagnetism are either single atoms or atomic ions, and it is precisely for such simple systems that the Zeeman effect can be calculated, the first order accurately and the second order approximately.

For the electrical case the situation is just the reverse. The interesting systems are those with permanent electric moments, and these are always molecules containing at least two atoms and often a much larger number. For such systems we are not able to solve Schrödinger's equation even in the absence of a field, much less to evaluate the Stark effect. The best one can do is to ignore the electronic structure of the molecule and represent it by a rigid structureless dipole. When we do this, we abandon all attempt to predict what the electric moment of a molecule should be, and have to content ourselves with correlating its unknown or assumed value with observable properties of matter.

Since then we can give a much deeper discussion of magnetic moments than of electric moments, we shall deal with magnetic moments first, contrary to the usual procedure. A common reason for treating electric moments first is that a classical treatment gives the right result. This is true, but the reason why is far from simple.

**§ 1405. Diamagnetism of atoms and atomic ions.** In considering the magnetic properties of free atoms or atomic ions, we naturally choose the nucleus as origin of coordinates. The diamagnetic term in the Hamiltonian of an atom or atomic ion in a specified quantum state is then according to (1402, 4)

$$\frac{H^2|e|^2}{8m_e c^2}\Sigma_e(x^2+y^2), \qquad (1405, 1)$$

where $-|e|$ denotes the charge and $m_e$ the mass of an electron, and the summation extends over all electrons. According to the theory of first order perturbations, the corresponding contribution to an energy level $\epsilon_{j,m}$ will be

$$\frac{H^2|e|^2}{8m_e c^2}\overline{\Sigma_e(x^2+y^2)}, \qquad (1405, 2)$$

where the average is evaluated by use of the eigen functions of the undisturbed degenerate state in the absence of the field. Since in the absence of a field there is no privileged direction, we can replace (2) by

$$\frac{H^2|e|^2}{8m_e c^2}\tfrac{2}{3}\overline{\Sigma_e r^2}, \qquad (1405, 3)$$

where $r$ denotes the distance of an electron from the nucleus.

The diamagnetic term in the moment of an atom or ion in the state $j$, $m$ is according to (1402, 6) obtained from (3) by means of the operation $-\partial/\partial H$. We thus obtain for the diamagnetic coefficient in (1402, 6)

$$b_{(d)} = b_{(d)j} = \frac{|e|}{6m_e c^2} \overline{\Sigma_e r^2}. \qquad (1405, 4)$$

As the averaging is performed over the configurations of the atom or ion in the absence of a field, $b_{(d)}$ is independent of $m$. We have therefore to average only over different values of $j$. The diamagnetic term $\kappa_d$ in the atomic susceptibility $\overline{\mu}/H$ is then by (1403, 14) given by

$$\kappa_d = -\Sigma_j b_{(d)j} \varpi_j e^{-\epsilon_j^0/kT}/\Sigma_j \varpi_j e^{-\epsilon_j^0/kT}. \qquad (1405, 5)$$

Usually only the normal electronic level contributes appreciably to the partition function. Alternatively if several levels contribute they will be members of the same spin multiplet and will have values of $\overline{\Sigma_e r^2}$ differing inappreciably from one another. Hence (5) reduces to

$$\kappa_d = -\frac{|e|}{6m_e c^2} \overline{\Sigma_e r^2}, \qquad (1405, 6)$$

where the averaging is performed *over the normal electronic level in the absence of a field*. The diamagnetic term in the atomic or ionic susceptibility was first calculated by Langevin by a classical treatment using Larmor's theorem. A quantal derivation of (6) by means of Larmor's theorem is also possible and is more usual than the derivation here given, which is due to Van Vleck.*

The first important prediction of formula (6) is that the diamagnetic contribution to the susceptibility is negative. Historically a substance was defined as diamagnetic when its susceptibility is negative, but the definition of diamagnetism, which we have chosen following Van Vleck, is preferable because for every substance there is a diamagnetic contribution to the susceptibility. The second prediction is that the diamagnetic contribution to the susceptibility is independent of temperature. Thirdly from (6) we shall be able to verify that when there is a paramagnetic term in the susceptibility it is usually about 1000 times greater than the diamagnetic term.

**§ 1406. Diamagnetic and paramagnetic substances.** For reasons that will appear later, the overwhelming majority of substances, apart from metals, consist of molecules or ions with no paramagnetic term in the susceptibility. These substances are referred to as diamagnetics. For polyatomic molecules or ions Larmor's theorem does not apply, nor can we obtain such a simple formula as (1405, 6) for the diamagnetic part of the

* For further details see Van Vleck, pp. 90–92.

molecular or ionic susceptibility. It can, however, be shown that the three most important deductions from (1405, 6) hold for all molecules and ions, but not for metallic electrons which will be discussed separately. Thus the diamagnetic term in the susceptibility is always negative; moreover, except for metals and semi-metallic substances such as bismuth, it is always independent of temperature, and the contribution per atom is about 1000 times smaller than the paramagnetic contribution of a typical paramagnetic atom.

The temperature independence of the susceptibility of diamagnetic substances was first established experimentally by P. Curie. Owing to this independence of temperature it is statistically of minor interest and we shall be chiefly concerned with paramagnetism.

A substance whose susceptibility contains a paramagnetic term as well as a diamagnetic is usually referred to as a paramagnetic. When one wants to compare a theoretically calculated value of the paramagnetic term in a susceptibility with an experimental value of a susceptibility of a paramagnetic substance, one must correct the experimental value by adding arithmetically the diamagnetic contribution. For any given paramagnetic atom or atomic ion, the diamagnetic contribution of this atom or ion will be negligible compared with its paramagnetic contribution, but it does not follow that one may neglect the total contribution of all the diamagnetic atoms or ions also present in the substance. A simple example will make this clear. In potassium ferric alum $KFe(SO_4)_2\,12H_2O$ the paramagnetism is entirely due to the $Fe^{+++}$ ion. To obtain an accurate experimental value of this paramagnetic ionic susceptibility, one should correct the observed molecular susceptibility of $KFe(SO_4)_2\,12H_2O$ by adding the numerical value of the molecular susceptibility of the diamagnetic substance ordinary alum $KAl(SO_4)_2\,12H_2O$. In this procedure we have justifiably ignored the diamagnetic contribution of the $Fe^{+++}$ ion, or rather the difference between this and that of the $Al^{+++}$ ion, but we have not ignored the appreciable diamagnetic contributions of the 47 other atoms in the molecule. Whenever a comparison is made between a theoretical and an experimental value of a paramagnetic susceptibility, it is to be presumed that the latter has been corrected in this way for the diamagnetic contribution.

**§ 1407. Linear Zeeman effect for atoms and atomic ions.** For a starting point in a statistical treatment of paramagnetism we require to know the coefficients of the linear and quadratic Zeeman effect. For single atoms and atomic ions these are known. The relevant quantum numbers of type $j$ for the atom in the absence of a field are $L$, $S$, $J$, with the following physical significance. In units $h/2\pi$ the orbital angular momentum is

$\{L(L+1)\}^{\frac{1}{2}}$, the spin angular momentum $\{S(S+1)\}^{\frac{1}{2}}$ and the resultant total angular momentum $\{J(J+1)\}^{\frac{1}{2}}$. There is also a quantum number $M$ of type $m$; that is to say the energy level for given $S$, $L$, $J$ is independent of $M$ in the absence of an external field. $M$ can have any of the $2J+1$ values $-J, (-J+1), \ldots, (J-1), J$. In a vanishingly small external magnetic field $H$ the component of the angular momentum parallel to the field is $M$ in the same units.

For an atom or ion in a singlet state $S = 0$ and $J = L$. There is no spin, and the ratio of the component of the magnetic moment along the field to that of the angular momentum in the same direction is $-|e|/2m_e c$, where $-|e|$ and $m_e$ are the charge and mass of the electron and $c$ is the velocity of light. The component of magnetic moment parallel to the field, for vanishingly small field, is therefore $M|e|h/4\pi m_e c$ or $M\beta$, where $\beta$ is *Bohr's magneton* defined by

$$\beta = \frac{|e|h}{4\pi m_e c} = 0{\cdot}917 \times 10^{-20}\,\text{ergs gauss}^{-1}. \qquad (1407, 1)$$

The corresponding linear Zeeman term in the energy is

$$a_{J,M}\,H = -M\beta H \quad (S=0, J=L). \qquad (1407, 2)$$

For an atom in an S state* $L = 0$ and $J = S$. The magnetic moment is entirely due to spin, and the ratio of its component in the direction of the field to that of the angular momentum in the same direction is $-|e|/m_e c$, double the value for a purely orbital magnetic moment. The magnetic moment parallel to the field, for vanishingly small field, is then $2M\beta$. The corresponding linear Zeeman effect is

$$a_{J,M}H = -2M\beta H \quad (L=0,\ J=S). \qquad (1407, 3)$$

For an atom in a $^1$S state we have $S = 0$, $L = 0$, $J = 0$ and consequently $M = 0$. For such an atom the linear Zeeman effect vanishes.

For an atom that is neither in a singlet state nor in an S state the magnetic moment is partly orbital and partly spin. Its component parallel to the magnetic field, for vanishingly small field, is $gM\beta$ and the corresponding linear Zeeman effect is

$$a_{J,M}H = -gM\beta H, \qquad (1407, 4)$$

where $g$ is Lande's splitting factor defined by

$$g = 1 + \frac{J(J+1) + S(S+1) - L(L+1)}{2J(J+1)}. \qquad (1407, 5)$$

We note that (2) and (3) are special cases of (4).

* The reader must remember that the letter S is used spectroscopically both to denote a type of atomic state ($L=0$) and to specify the resultant electron spin $S$, but this should not cause confusion.

**§ 1408. Quadratic Zeeman effect.** The quadratic Zeeman effect consists of two terms. There is a paramagnetic term $\frac{1}{2}b_{(p)}H^2$, which is the second order perturbation corresponding to the first order perturbation described in the preceding section. There is also a diamagnetic term $\frac{1}{2}b_{(d)}H^2$ already discussed in § 1405. We can now verify that for a paramagnetic atom or atomic ion the diamagnetic term $\kappa_d$ in the susceptibility is negligible compared with the paramagnetic term $\kappa_p$. From (1403, 14) we see that the order of magnitude of the ratio is

$$-\frac{\kappa_p}{\kappa_d} \simeq \frac{a^2_{J,M}}{kT} : -b_{(d)} \simeq \frac{\beta^2}{kT} : \frac{|e|^2\overline{r^2}}{m_e c^2} \simeq \frac{|e|^2 h^2}{m_e^2 c^2 kT} : \frac{|e|^2 \overline{r^2}}{m_e c^2} \simeq \frac{h^2}{m_e \overline{r^2} kT}, \quad (1408, 1)$$

using (1407, 4), (1405, 4) and (1407, 1). But we can define a rough average orbital velocity $\bar{v}$ by

$$m_e \bar{v}\bar{r} \simeq h. \quad (1408, 2)$$

Substituting from (2) into (1), we find*

$$-\frac{\kappa_p}{\kappa_d} \simeq \frac{m_e \bar{v}^2}{kT} \simeq \frac{\text{orbital kinetic energy}}{\text{thermal energy}} \simeq \frac{10^5}{T}, \quad (1408, 3)$$

so that at ordinary temperatures $-\kappa_d/\kappa_p \simeq 10^{-3}$. This justifies our ignoring the diamagnetic contribution to the susceptibility of a paramagnetic atom or atomic ion.

We have still to consider the paramagnetic term $\frac{1}{2}b_{(p)}H^2$ in the Zeeman effect. Its evaluation has been performed by Van Vleck† and is not simple. We shall not consider it in detail. According to spectroscopic standards the term is small for ordinarily available field strengths, and so difficult to observe. This smallness is, however, due to the factor $H^2$. It does not follow that the term in the susceptibility due to $b_{(p)}$ is always negligible. The important feature of the explicit formula for $b_{(p)}$ is that its denominator contains as a factor the energy of separation between the given $J$ level for zero field and its neighbouring $J$ level or levels. The greater these energy separations the smaller will be $b_{(p)}$. *If the energy separation between the normal state and the next higher state of the multiplet is large compared with $kT$, the contribution of $b_{(p)}$ to the susceptibility will be unimportant, if not entirely negligible.* When this condition is not satisfied the contribution of $b_{(p)}$ must be carefully considered.

**§ 1409. Paramagnetism of atoms and atomic ions.** When we neglect the diamagnetic term in the atomic susceptibility, we have according to (1403, 14) for the atomic or ionic paramagnetic susceptibility

$$\kappa_p = \Sigma_J e^{-\epsilon_J^0/kT} \Sigma_M \left\{ \frac{a^2_{J,M}}{kT} - b_{(p)J,M} \right\} \Big/ \Sigma_J (2J+1) e^{-\epsilon_J^0/kT}, \quad (1409, 1)$$

* This instructive formula is taken from a lecture by Darwin.

† Van Vleck, pp. 173–175.

since $\varpi_J = 2J+1$, this being the number of possible values of $M$ for given $J$. The further reduction of (1409, 1) depends greatly on the energy separation between the states of different $J$. It often, but not always, happens that the normal electronic level is separated from the next level of the multiplet by an energy difference large compared with $kT$. In such cases (1) simplifies in two respects. Firstly we may replace the sums $\Sigma_J$ by their first terms and secondly we may omit the term in $b_{(p)}$, as explained in the preceding section. Formula (1) then reduces to

$$\kappa_p = \frac{\Sigma_M a_{J,M}^2}{(2J+1)kT} = \frac{g^2\beta^2}{kT}\frac{\sum_{M=-J}^{+J} M^2}{2J+1} = \frac{J(J+1)g^2\beta^2}{3kT}. \quad (1409, 2)$$

Formula (2) is due to Hund* and is a special case of the relation

$$\kappa_p \propto 1/T, \quad (1409, 3)$$

discovered experimentally by P. Curie, and known as *Curie's law*.

When the condition that the energy separation is large compared with $kT$ is not fulfilled, we not only have to include higher terms besides the normal term in (1) but we must also retain the temperature independent term $b_{(p)J,M}$. In this case formula (1) becomes

$$\kappa_p = \frac{\Sigma_J\{g_J^2\beta^2 J(J+1)/3kT + b_J\}(2J+1)e^{-\epsilon_J^0/kT}}{\Sigma_J(2J+1)e^{-\epsilon_J^0/kT}}, \quad (1409, 4)$$

where $b_J$ is an atomic quantity characteristic of the particular state $J$. Formula (4) is due to Van Vleck, who also evaluated $b_J$. The form of $b_J$ is not simple, and we shall not give details of it. Fortunately in most applications the energy of separation between the two lowest $J$ states is large compared with $kT$, so that one may use Hund's much simpler formula (2). Many general readers will be content to know under what conditions Hund's formula becomes inaccurate without troubling themselves with the details of Van Vleck's more general formula. Those who are interested in these details cannot do better than read Van Vleck's own account.†

§ 1410. **Spectroscopic stability.** Before we apply formula (1409,2), it is of interest to consider its forms in more detail. The quantity $M$ is a measure in units of $h/2\pi$ of the angular momentum about the field. The factor $\sum_{M=-J}^{+J} M^2/(2J+1)$ therefore denotes the square of this component of angular momentum averaged over all values of $M$. On evaluating the sum, this average value is found to be $\frac{1}{3}J(J+1)$ or one-third of the square of the total angular momentum. If then we denote by $\theta$ the angle between the resultant angular momentum $J$ and the field, we see that the average value

* Hund, *Zeit. Phys.* **33**, 855 (1925). † Van Vleck, pp. 232–238.

of $\cos^2\theta$ for all values of $M$ is $\frac{1}{3}$. But the classical average value of $\cos^2\theta$ over all directions in space when we ignore quantization is also $\frac{1}{3}$. We see then that we obtain the same average value for $M^2$, whether we average over the actual quantized values of $M$ for a given $J$ or classically over all directions. This agreement between the two ways of averaging is not accidental, but is a consequence of *the principle of spectroscopic stability*.*

According to this principle, the average over all values of $M$ for given $J$ of the square of any vector is unaltered by any perturbation whatever. Hence the average of $\cos^2\theta$ over all $M$ for given $J$ is the same for a finite field as for vanishing field. But for vanishing field there is no privileged direction and this average must be the same about any one of three directions at right angles to one another. The sum of these three averages is 1 and so each average is $\frac{1}{3}$.

We have already implicitly used the principle of spectroscopic stability in discussing diamagnetism, when we replaced $\overline{x^2+y^2}$ by $\frac{2}{3}\overline{r^2}$.

§ **1411. Langevin's formula.** Owing to the principle of spectroscopic stability we can often obtain correct results by applying a semi-classical treatment to an appropriate model. A consistently classical treatment of any system of electrons leads to zero magnetic susceptibility.† This correct result, which may at first seem surprising, is not so difficult to accept when one remembers that on purely classical theory a stable electronic atom does not exist. To obtain positive results by classical methods one has to postulate the stability of stationary states, and this is equivalent to assuming some kind of quantization. It is therefore more accurate to call such a treatment semi-classical than classical.

The treatment which we are about to outline is due to Langevin.‡ It is not strictly classical since it postulates definite stationary states of the atom, which is taken to be a rigid atomic magnet with a permanent moment $\mu_0$. Its energy in a magnetic field $H$ with which it makes an angle $\theta$ is $-\mu_0 H\cos\theta$. If all values of $\theta$ are allowable, the orientational factor $O(T)$ in the partition function is

$$O(T) = \int_0^\pi e^{\mu_0 H\cos\theta/kT}\, 2\pi\sin\theta\, d\theta$$

$$= 2\pi\frac{kT}{\mu_0 H}\int_{-\mu_0 H/kT}^{\mu_0 H/kT} e^{\xi}\, d\xi = 4\pi\frac{kT}{\mu_0 H}\sinh\frac{\mu_0 H}{kT}. \quad (1411, 1)$$

For the average component of the moment along the field we deduce,

* See Van Vleck, p. 111 and pp. 137–142.

† See Van Vleck, pp. 94–100.

‡ See Stoner, pp. 110–114.

using (1403, 8),

$$\bar{\mu} = kT\frac{\partial \log O(T)}{\partial H} = \mu_0\left(\coth\frac{\mu_0 H}{kT} - \frac{kT}{\mu_0 H}\right) = \mu_0 L\left(\frac{\mu_0 H}{kT}\right), \quad (1411, 2)$$

where $L(x)$, called *Langevin's function*, is defined by

$$L(x) = \coth x - 1/x. \quad (1411, 3)$$

Even for the highest fields available at ordinary temperatures $\mu_0 H/kT \ll 1$, and we may therefore replace (1) by

$$O(T) = 4\pi\{1 + \tfrac{1}{6}\mu_0^2 H^2/k^2T^2\}, \quad (1411, 4)$$

and (2) by

$$\bar{\mu} = \mu_0^2 H/3kT. \quad (1411, 5)$$

We therefore have

$$\kappa_p = \bar{\mu}/H = \mu_0^2/3kT. \quad (1411, 6)$$

If we now replace $\mu_0^2$ in (6) by its quantal value $g^2J(J+1)\beta^2$, we recover Hund's formula (1409, 2).

§ **1412. Effective magneton numbers.** As Langevin's semi-classical formula was already familiar at the time when Hund obtained its quantal analogue (1409, 2), it is still customary to apply to Hund's formula a terminology more suitable to Langevin's. In this terminology the effective moment $\mu_{\text{eff}}$ is defined by

$$\mu_{\text{eff}} = \{3kT\kappa_p\}^{\frac{1}{2}}, \quad (1412, 1)$$

so that according to Langevin's model $\mu_{\text{eff}}$ is the same as $\mu_0$. When Hund's formula (1409, 2) is applicable, we have

$$\mu_{\text{eff}}/\beta = g\{J(J+1)\}^{\frac{1}{2}}. \quad (1412, 2)$$

The ratio $\mu_{\text{eff}}/\beta$ is called *the effective magneton number*. It should be noticed that the effective magneton number is not integral, nor even rational.

When Hund's formula (1409, 2) is not applicable, the theoretical value for $\mu_{\text{eff}}/\beta$ is obtained by substituting into (1) the theoretical value of $\kappa_p$ given by Van Vleck's formula (1409, 4). In this case the effective magneton number is a complicated quantity, and is not equal to the number of Bohr magnetons in the magnetic moment of a stationary state.

§ **1413. Ions of rare earth elements.** The whole theoretical treatment outlined above assumes the absence of appreciable interaction between the paramagnetic atoms or ions. Owing to the difficulty of obtaining paramagnetic substances in the vapour state, the most suitable substances on which to test the theory are solutions or solid hydrated forms of salts containing an atomic ion which is not in a $^1S$ state. Such ions are formed by the transition elements of the Fe, Pd and Pt series and by the elements of the rare earth group. We shall consider the latter first.

Measurements have been made of the susceptibilities of the solid hydrated sulphates of almost all the rare earth elements in the trivalent state. In this series of trivalent ions, the first $La^{+++}$ has no $4f$ electrons, while the last $Lu^{+++}$ has a complete group of 14. The hydrated sulphates of both these ions are found to be diamagnetic in agreement with theory. This observed diamagnetic susceptibility is arithmetically added to the susceptibility of the hydrated sulphates of the remaining metals to obtain the paramagnetic

TABLE 1

*Calculated and observed effective magneton numbers for the atomic ions of the rare earth metals*

| Ion | No. of $4f$ electrons | Normal state | $S$ | $L$ | $J$ | $g$ | Effective magneton numbers | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | Calc. Hund | Calc. Van Vleck | Obs.* |
| $La^{+++}$ | 0 | $^1S_0$ | 0 | 0 | 0 | — | 0 | 0·00 | 0 |
| $Ce^{+++}$ | 1 | $^2F_{\frac{5}{2}}$ | $\frac{1}{2}$ | 3 | $\frac{5}{2}$ | $\frac{6}{7}$ | 2·54 | 2·56 | 2·4 |
| $Pr^{+++}$ | 2 | $^3H_4$ | 1 | 5 | 4 | $\frac{4}{5}$ | 3·58 | 3·62 | 3·5 |
| $Nd^{+++}$ | 3 | $^4I_{\frac{9}{2}}$ | $\frac{3}{2}$ | 6 | $\frac{9}{2}$ | $\frac{8}{11}$ | 3·62 | 3·68 | 3·5 |
| $Il^{+++}$ | 4 | $^5I_4$ | 2 | 6 | 4 | $\frac{3}{5}$ | 2·68 | 2·83 | — |
| $Sm^{+++}$ | 5 | $^6H_{\frac{5}{2}}$ | $\frac{5}{2}$ | 5 | $\frac{5}{2}$ | $\frac{2}{7}$ | 0·84 | 1·55, 1·65 | 1·5 |
| $Eu^{+++}$ | 6 | $^7F_0$ | 3 | 3 | 0 | — | 0 | 3·40, 3·51 | 3·6 |
| $Gd^{+++}$ | 7 | $^8S_{\frac{7}{2}}$ | $\frac{7}{2}$ | 0 | $\frac{7}{2}$ | 2 | 7·94 | 7·94 | 8·0 |
| $Tb^{+++}$ | 8 | $^7F_6$ | 3 | 3 | 6 | $\frac{3}{2}$ | 9·72 | 9·7 | 9·5 |
| $Ds^{+++}$ | 9 | $^6H_{\frac{15}{2}}$ | $\frac{5}{2}$ | 5 | $\frac{15}{2}$ | $\frac{4}{3}$ | 10·65 | 10·6 | 10·7 |
| $Ho^{+++}$ | 10 | $^5I_8$ | 2 | 6 | 8 | $\frac{5}{4}$ | 10·61 | 10·6 | 10·3 |
| $Er^{+++}$ | 11 | $^4I_{\frac{15}{2}}$ | $\frac{3}{2}$ | 6 | $\frac{15}{2}$ | $\frac{6}{5}$ | 9·58 | 9·6 | 9·5 |
| $Tu^{+++}$ | 12 | $^3H_6$ | 1 | 5 | 6 | $\frac{7}{6}$ | 7·56 | 7·6 | 7·3 |
| $Yb^{+++}$ | 13 | $^2F_{\frac{7}{2}}$ | $\frac{1}{2}$ | 3 | $\frac{7}{2}$ | $\frac{8}{7}$ | 4·54 | 4·5 | 4·5 |
| $Lu^{+++}$ | 14 | $^1S_0$ | 0 | 0 | 0 | — | 0 | 0·00 | 0 |

* These values are averages given by Stoner of various experimental values, some on solid hydrated sulphates, others on aqueous solutions of sulphates or nitrates. For more detailed values, see Van Vleck, p. 243.

contribution of the trivalent ion. The value can then be compared with the theoretical value given by Hund's formula (1409, 2) or Van Vleck's formula (1409, 4). The relevant data are collected in Table 1. The normal states are those derived from general spectroscopic laws for the specified numbers of $4f$ electrons. Although they have not been checked spectroscopically, they are not open to doubt. It will be seen that except for $Sm^{+++}$ and $Eu^{+++}$ the differences between the values given by Hund's and Van Vleck's formulae are insignificant, and there is good agreement between these values and those found experimentally. For $Sm^{+++}$ and $Eu^{+++}$ the experimental values

are in good agreement with Van Vleck's formula, but not with Hund's. The alternative values for $Sm^{+++}$ and $Eu^{+++}$ obtained from Van Vleck's formula are due to two different estimates of the screening constant for $4f$ electrons, this quantity being required in calculating the multiplet intervals.

The conditions under which separations between the terms of a multiplet can become especially small are large $S$, large $L$ and small $J$. As $Gd^{+++}$ is in an S state, there is no multiplet. The conditions just mentioned are most perfectly fulfilled by the immediate neighbours of $Gd^{+++}$, namely $Eu^{+++}$ and $Tb^{+++}$. The multiplet of $Eu^{+++}$ is normal and the small separations

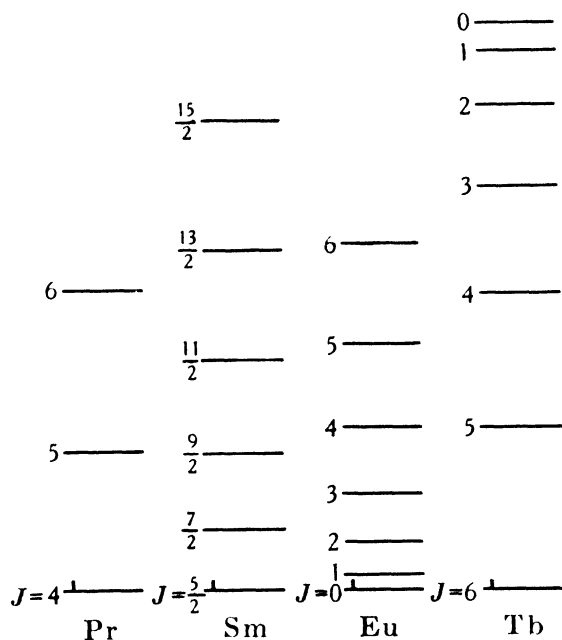



Fig. 1. Electronic energy levels of trivalent ions of elements Pr(59), Sm(62), Eu(63), Tb(65). The vertical bar on the lowest levels gives the energy scale. Its length corresponds approximately to 200 wave numbers, or to $kT$ at 300° K.

occur between the low terms of the multiplet, but the multiplet of $Tb^{+++}$ is inverted and the small separations occur between the high terms of the multiplet; the separation between the two lowest terms, which are the ones that matter, is large and so Hund's formula is accurate for $Tb^{+++}$. The multiplet separations for four characteristic ions are shown schematically in Fig. 1. It is evident from the figure that deviations from Hund's formula will be greatest for $Eu^{+++}$, and may be appreciable for $Sm^{+++}$, as in fact they are.

The comparison between theory and experiment for the ions of the rare earths is summarised in Fig. 2. From the excellent agreement we conclude that the magnetic properties of these ions in the hydrated solid salts and in solution are the same as those of the free gaseous ions. The reason is certainly because the incomplete group of $4f$ electrons, to which the paramagnetism is due, is so deeply buried in the atomic core.

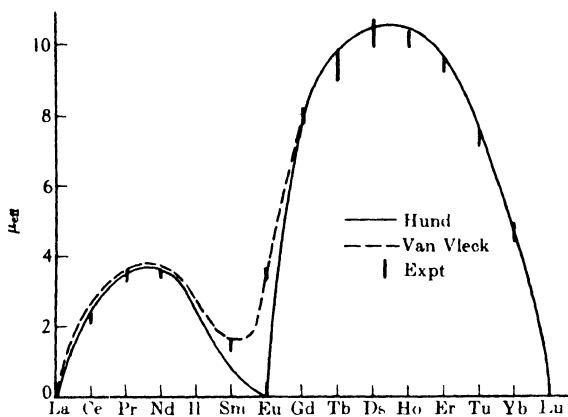



Fig. 2. Theoretical and experimental values of effective magneton numbers of rare earth ions at ordinary temperatures.

§ 1414. **Ions of transition elements.** When similar comparisons are made for salts of transition elements between the observed effective magneton numbers and those calculated from Hund's formula, there is no agreement except for $Mn^{++}$ and $Fe^{+++}$. Nor is the agreement improved by taking account of the higher terms of the multiplet. The fact that the only two ions, $Mn^{++}$ and $Fe^{+++}$, for which there is agreement, are in S states suggests that the orientatable element in these ions is the electron spin, and that the orbital angular momentum is "quenched" by the interaction with the field of the surrounding atoms which has not spherical symmetry. This suggestion is due to Stoner. The incomplete group of $3d$ electrons is here the outermost group in the atom, and is not well screened from the neighbouring ions as is the $4f$ group in the rare earths by the completed $5s$ and $5p$ groups. It can be shown theoretically* that the orbital magnetic moment will actually be quenched in this way, leaving the spin moment unaffected, provided that the asymmetrical fields acting on the ion are sufficiently strong.

Assuming then that this quenching of the orbital angular momentum

* See Van Vleck, p. 287.

does occur, we derive the theoretical values by setting $L = 0$, $J = S$, $g = 2$ in Hund's formula (1409, 2). We thus obtain Stoner's formula

$$\kappa_p = 4S(S+1)\beta^2/3kT. \tag{1414, 1}$$

This leads to an effective magneton number

$$\mu_{\text{eff}}/\beta = 2\{S(S+1)\}^{\frac{1}{2}}. \tag{1414, 2}$$

The data for comparison between theory and experiment are given in Table 2. The observed values quoted were obtained by experiments on

TABLE 2

*Calculated and observed effective magneton numbers of ions of the transition elements of the iron group*

| Ion | No. of 3*d* electrons | Normal state | $S$ | $L$ | $J$ | $g$ | Effective magneton numbers | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | Calc. Hund | Calc. Van Vleck | Calc. Stoner | Obs.* |
| $K^+, \ldots V^{5+}$ | 0 | $^1S_0$ | 0 | 0 | 0 | — | 0 00 | 0·00 | 0·00 | 0·00 |
| $Sc^{++}$<br>$Ti^{+++}$<br>$V^{++++}$ | 1 | $^2D_{\frac{3}{2}}$ | $\frac{1}{2}$ | 2 | $\frac{3}{2}$ | $\frac{4}{5}$ | 1 55 | 2·57<br>2·18<br>1·78 | 1·73 | 1 75 |
| $Ti^{++}$<br>$V^{+++}$ | 2 | $^3F_2$ | 1 | 3 | 2 | $\frac{2}{3}$ | 1·63 | 3·36<br>2·73 | 2·83 | <br>2 76–2·85 |
| $V^{++}$<br>$Cr^{+++}$<br>$Mn^{++++}$ | 3 | $^4F_{\frac{3}{2}}$ | $\frac{3}{2}$ | 3 | $\frac{3}{2}$ | $\frac{2}{5}$ | 0·77 | 3·60<br>2·97<br>2·47 | 3·87 | 3·81–3·86<br>3·68–3·86<br>4·00 |
| $Cr^{++}$<br>$Mn^{+++}$ | 4 | $^5D_0$ | 2 | 2 | 0 | — | 0·00 | 4·25<br>3·80 | 4·90 | 4·80 |
| $Mn^{++}$<br>$Fe^{+++}$ | 5 | $^6S_{\frac{5}{2}}$ | $\frac{5}{2}$ | 0 | $\frac{5}{2}$ | 2 | 5·92 | 5·92<br>5·92 | 5·92 | 5·2–5·96<br>5·94 |
| $Fe^{++}$ | 6 | $^5D_4$ | 2 | 2 | 4 | $\frac{3}{2}$ | 6·70 | 6·54 | 4·90 | 5·33 |
| $Co^{++}$ | 7 | $^4F_{\frac{9}{2}}$ | $\frac{3}{2}$ | 3 | $\frac{9}{2}$ | $\frac{4}{3}$ | 6·64 | 6·56 | 3·87 | 4·6–5·0 |
| $Ni^{++}$ | 8 | $^3F_4$ | 1 | 3 | 4 | $\frac{5}{4}$ | 5·59 | 5·56 | 2·83 | 3·23 |
| $Cu^{++}$ | 9 | $^2D_{\frac{5}{2}}$ | $\frac{1}{2}$ | 2 | $\frac{5}{2}$ | $\frac{6}{5}$ | 3·55 | 3·53 | 1·73 | 1·8–2·0 |
| $Cu^+$, $Zn^{++}$ | 10 | $^1S_0$ | 0 | 0 | 0 | — | 0·00 | 0·00 | 0·00 | 0·00 |

* The experimental values are taken from Van Vleck, p. 285. They are for aqueous solutions. Values for the solid salts do not differ greatly from those for solutions.

aqueous solutions at ordinary temperatures. Almost identical values are obtained from hydrated solid salts. It will be seen that the agreement between the experimental values of the effective magneton numbers and the values calculated by (2) is satisfactory in most cases. There are, however, real discrepancies, notably for $Co^{++}$, the significance of which is discussed in the next section.

**§ 1415. Effect of crystalline field.** Strictly the electric field due to the surrounding ions and molecules in the crystal always has some perturbing effect on the states of the paramagnetic ions, but this perturbation may be important in some cases and negligible in others. This perturbation is conveniently referred to as *the crystalline Stark effect.* There are actually two such effects: the one is a direct effect on the orbital momentum of the magnetic ion; the other is an indirect effect on the spin momentum through the coupling between the spin and the orbital angular momentum. This indirect effect on the spins is much weaker than the direct effect on the orbitals, and is negligible except at temperatures of the order 1° K. or below. We shall discuss it briefly in § 1434, but here we ignore it and confine ourselves to a qualitative description of the direct effect on the orbitals.

The effect of the crystalline field is to split each degenerate energy level into several levels, thus reducing and sometimes removing the degeneracy. Since ions in S states have no degeneracy, apart from that of spin which we are here neglecting, it follows that there is no crystalline Stark effect for these ions. The theory of § 1413 should therefore be particularly accurate for $Gd^{+++}$, as is in fact the case, Curie's law remaining accurate down to the temperature of liquid helium. For ions not in S states the nature of the crystalline Stark effect varies according to the intensity of the crystalline field.

In the ions of the rare earths, since the *f*-electrons involved are deep in the core of the ion, the effect is a comparatively weak one, the energy of interaction with the crystalline field being small compared with the multiplet separations in the free ion. Each $J$ level is split into two or more levels, the nature and extent of the splitting depending on the value of $J$ and the symmetry of the crystalline field around the ion, which is not necessarily the same as the symmetry of the whole crystal. Generally speaking the splitting is of the same order of magnitude as $kT$ at ordinary temperatures and should not be neglected. The effect of this splitting on the susceptibilities varies individually from one ion to another and for details we refer the reader to an excellent summarizing report by Van Vleck.* Here we have space only for two rather general remarks. There is usually a wide range of temperatures through which the ionic paramagnetic susceptibility may be expressed empirically in the form

$$\kappa_p = \frac{J(J+1)\,g^2\beta^2}{3k(T-\Theta_W)}, \qquad (1415, 1)$$

where $\Theta_W$ is an empirical constant (positive or negative) having the dimensions of temperature. We observe that formula (1) differs from Hund's

* Van Vleck, *Conference on Magnetism* (Strasbourg, 1939).

formula (1409, 2) in the substitution of $T - \Theta_W$ for $T$. A substitution of this form was first used by Weiss in the theory of ferromagnetism (see § 1446) and for this reason the relation

$$\kappa_p \propto 1/(T - \Theta_W) \qquad (1415, 2)$$

is called *Weiss' law*. For $\Theta_W = 0$ Weiss' law (2) reduces to Curie's law (1409, 3). We would emphasize that formula (1) loses it validity at temperatures below about 100° K. Our second remark of a general nature refers to a theorem due to Kramers.* According to this theorem, when the crystalline field splits the (orbital) states of an ion (or atom) having an odd number of electrons, the energy levels still remain at least doubly degenerate; for an ion (or atom) having an even number of electrons a sufficiently unsymmetrical field will completely remove the degeneracy (apart from that

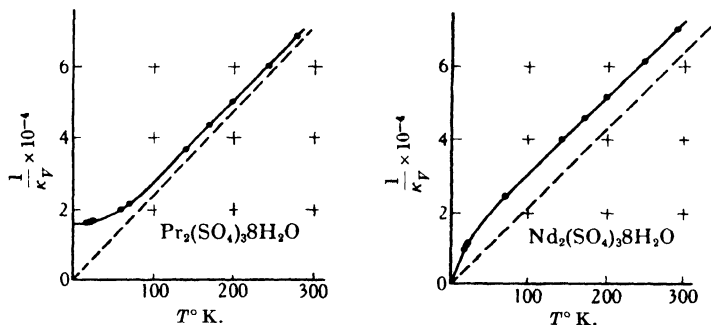



Fig. 3. Dependence on temperature of the volume susceptibility $\kappa_V$ (per cm.³) of the hydrated sulphates of praseodymium and neodymium.
Theoretical curves according to Penney and Schapp, *Phys. Rev.* **41**, 194 (1932). Experimental data of Gorter and De Haas, *Comm. Phys. Lab. Leiden*, no. 218*b* (1931).

of spin). As a consequence of this there is a striking difference at low temperatures between the behaviour of ions with an odd and ions with an even number of electrons. This difference is clearly illustrated in Fig. 3, which shows the calculated and observed susceptibilities of the hydrated sulphates of praseodymium and of neodymium. As $T \to 0$ the susceptibility of praseodymium tends to a finite limit, whereas that of neodymium tends to infinity. Actually other phenomena intervene before the limit $T = 0$ is reached (see § 1433). The straight portions of both curves correspond to a formula of the form (1) with a negative value of $\Theta_W$. For a detailed discussion of all the rare earth ions the reader should refer to Van Vleck's report.

In the ions of the transition elements the crystalline field acts on the $d$-electrons which lie much less deep than the $f$-electrons of the rare earth ions, and consequently the interaction energy with the crystalline field is

* Kramers, *Proc. Sec. Sci. Amsterdam*, **33**, 959 (1930).

comparatively great, being equal to $kT$ with $T$ of the order $10^5$ deg., and so greater than the separation between the terms of the multiplet of the free ion. This field destroys the (Russell-Saunders) coupling between the orbital angular momentum determined by $L$ and the spin angular momentum determined by $S$. When we neglect the indirect effect on the spin, which is negligible except at liquid helium temperatures, the effect is to split the energy level into $2L+1$ levels. Thus an S term ($L=0$) is unaffected; a D term ($L=2$) is split into five levels; an F term ($L=3$) is split into seven levels. The extent and details of the splitting depend very much on the symmetry of the crystalline field. If the field had cubic symmetry, a D term would be split only into a doubly degenerate level and triply degenerate level; under the same conditions an F term would be slit into one non-degenerate and two triply degenerate levels. A higher degree of asymmetry is required to remove the degeneracy completely. A non-degenerate energy level behaves as an S term. If the separation between the lowest non-degenerate level and the next lowest is great compared with $kT$, the orbital contribution to the magnetic moment is effectively quenched.

It has been proved by Jahn and Teller* that every stable state of a non-linear polyatomic molecule is orbitally non-degenerate, and every molecule will automatically adjust its shape so as to destroy any degeneracy due to symmetry. In the alums, the compounds on which most magnetic measurements have been made, we may regard the paramagnetic ion and its six surrounding water molecules as a complex molecule. According to the crystal structure of the alums as determined by X-rays, the crystal as a whole has cubic symmetry, but the symmetry about a single paramagnetic ion is trigonal. Even trigonal symmetry is too high to remove completely the orbital degeneracy of the ions, but in such a case the water molecules become displaced so that the symmetry is further reduced and the degeneracy completely removed; owing to resonance between the unsymmetrical configurations, the X-ray analysis shows an (average) cubic symmetry. This rather complicated reasoning leads to the conclusion that the crystalline field around a paramagnetic ion in an alum has nearly cubic symmetry and still more nearly trigonal symmetry, but strictly still lower symmetry. When a field of cubic symmetry would suffice to give a lowest state which is orbitally non-degenerate, and separated from the next higher state by an interval large compared with $kT$, the theory of § 1414 should apply with a high degree of accuracy. This is the case both according to theory and experiment for $Ni^{++}$ and $Cr^{+++}$. The theory is also accurate for ions in S states such as $Mn^{++}$ and $Fe^{+++}$. On the other hand, when a cubic field is insufficient to remove the degeneracy, since the actual asymmetry of the field is certainly

* Jahn and Teller, *Proc. Roy. Soc.* A, **161**, 220 (1937).

small, the separation between the lowest level and the next lowest may be comparable with $kT$. In such a case the behaviour of the susceptibility will be much more complicated, Curie's law will not be obeyed and Stoner's formula will be inaccurate. This is the case, both according to experiment and theory, in a most marked degree for $Co^{++}$. We have merely given this brief qualitative summary to explain why the very simple theory of § 1414 is sufficiently accurate for some ions, but entirely inadequate for others. For all details of the theory and of the experimental data the reader is referred to Van Vleck's report.

**§ 1416. Magnetic saturation at low temperatures.** Hitherto we have assumed throughout that $\beta H/kT \ll 1$. This condition is satisfied for all paramagnetic substances at ordinary temperatures even at the highest available field strengths. We can, however, realize departures from the condition $\beta H/kT \ll 1$ by the simultaneous use of strong fields and low temperatures. One then obtains *saturation effects*, when the excess of the fraction of magnetic ions (or atoms) parallel to the field over the fraction antiparallel to the field becomes comparable with unity. Owing to the necessity of using low temperatures, such saturation effects will usually be complicated by the crystalline Stark effect. We shall accordingly confine our discussion to ions in an S state, for which this effect is absent.

We shall use formula (1403, 3) to obtain the required partition function. But the only relevant terms in the partition function $f(T)$ for an unexcited monatomic ion compose an electronic factor $e(T)$ which takes account of all the possible orientations of the ion relative to the field. For an ion in a $^{2S+1}S$ state the magnetic quantum number $M$ can take the values $-S$, $-S+1, \ldots, S-1, S$. For given $M$ the magnetic moment is $2M\beta$ and the energy in the field is $-2M\beta H$. Consequently we have

$$e(T) = \sum_{M=-S}^{S} e^{2M\beta H/kT}. \qquad (1416, 1)$$

The series in (1) is a geometrical progression; on summing the series we obtain

$$e(T) = \frac{e^{(2S+1)\beta H/kT} - e^{-(2S+1)\beta H/kT}}{e^{\beta H/kT} - e^{-\beta H/kT}} = \frac{\sinh\{(2S+1)\beta H/kT\}}{\sinh\{\beta H/kT\}}. \qquad (1416, 2)$$

Hence, using (1403, 8), we derive from (2)

$$\frac{\bar{\mu}}{\beta} = \frac{kT}{\beta}\frac{\partial \log e(T)}{\partial H} = (2S+1)\coth\left\{\frac{(2S+1)\beta H}{kT}\right\} - \coth\left\{\frac{\beta H}{kT}\right\}. \qquad (1416, 3)$$

For small values of $\beta H/kT$ formula (3) reduces to

$$\frac{\bar{\mu}}{\beta} = \frac{4S(S+1)\beta H}{3kT} \quad (\beta H/kT \ll 1), \qquad (1416, 4)$$

in agreement with (1409, 2). In the opposite extreme of large $\beta H/kT$ formula (3) becomes

$$\bar{\mu}/\beta = 2S \quad (\beta H/kT \gg 1). \qquad (1416, 5)$$

We thus see that as $H$ increases $\bar{\mu}$ approaches a saturation value $\mu_0$ given by

$$\mu_0 = 2S\beta. \qquad (1416, 6)$$

Substituting (6) into (3), we obtain

$$\frac{\bar{\mu}}{\mu_0} = \frac{2S+1}{2S}\coth\left\{\frac{2S+1}{2S}\frac{\mu_0 H}{kT}\right\} - \frac{1}{2S}\coth\left\{\frac{1}{2S}\frac{\mu_0 H}{kT}\right\}. \qquad (1416, 7)$$

These formulae are due to Brillouin, and the right side of (7) regarded as a function of $\mu_0 H/kT$ is called *Brillouin's function*. There are various Brillouin functions for various values of $S$. If we make $S \to \infty$, then Brillouin's function becomes Langevin's function $L(\mu_0 H/kT)$ defined by (1411, 3).

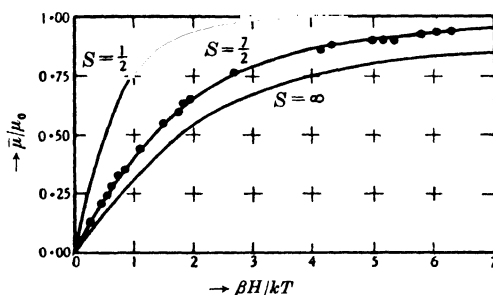



Fig. 4. Magnetic saturation at high fields and low temperatures. The theoretical curves are the Brillouin functions for $S = \frac{1}{2}$, $S = \frac{7}{2}$ and the Langevin function for $S = \infty$. The points denote the experimental data of Woltjer and Kamerlingh Onnes for the hydrated sulphate of gadolinium.

For an atom or ion in a $^2$S state we have $S = \frac{1}{2}$ and Brillouin's formula (7) reduces to

$$\frac{\bar{\mu}}{\mu_0} = 2\coth\left\{\frac{2\mu_0 H}{kT}\right\} - \coth\left\{\frac{\mu_0 H}{kT}\right\} = \tanh\left\{\frac{\mu_0 H}{kT}\right\}. \qquad (1416, 8)$$

In Fig. 4 we show Brillouin's functions for $S = \frac{1}{2}$ and for $S = \frac{7}{2}$, together with Langevin's function ($S = \infty$). The gadolinium ion is in an $^8$S state and the appropriate theoretical curve is therefore the one for $S = \frac{7}{2}$. The experimental data of Woltjer and Onnes* on hydrated gadolinium sulphate are shown in the diagram to be in complete agreement with the theory.

* Woltjer and Onnes, *Comm. Phys. Lab. Leiden*, no. 167c (1923).

**§ 1417. Other paramagnetic molecules.** We have seen that the orbital angular momentum is quenched by the lack of spherical symmetry in the crystalline field of salts of the transition elements. It is also quenched in a somewhat similar manner in all polyatomic molecules except linear molecules, which can have angular momentum with a permanent component about the line of nuclei. Actually the only definitely known example is NO, which has both orbital and spin angular momenta. Both contribute to the paramagnetism and the theory is not simple. The normal electronic state is $^2\Pi_{\frac{1}{2}}$, but the upper term $^2\Pi_{\frac{3}{2}}$ of the multiplet is separated by an energy difference which is equal to $kT$ at $T = 179°$ K., and so is comparable with $kT$ at ordinary temperatures. It is therefore necessary to take account of

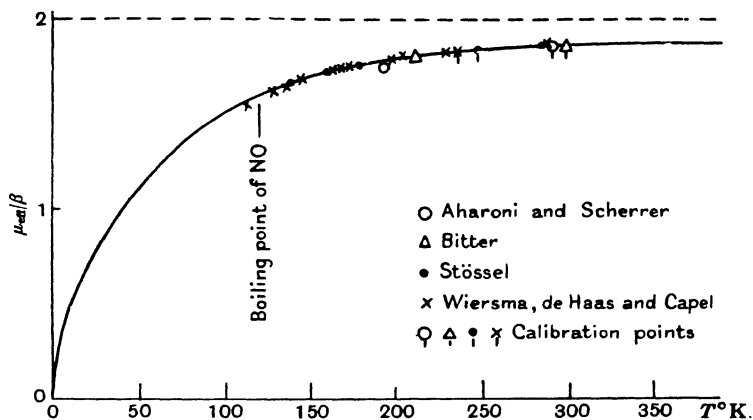



Fig. 5. The theoretical and experimental values of the effective magneton number of NO. Theoretical curve corresponds to Van Vleck's formula (1417, 1).

the equilibrium distribution between the two states of the doublet, and also to include terms of the quadratic Zeeman effect which are not negligible. The formula obtained by Van Vleck* for the effective magneton number is

$$\frac{\mu_{eff}}{\beta} = 2\left\{\frac{1 - e^{-\Theta/T} + e^{-\Theta/T}\Theta/T}{(1 + e^{-\Theta/T})\,\Theta/T}\right\}^{\frac{1}{2}}, \tag{1417, 1}$$

where $\Theta$ ( = 179) is the energy separation of the doublet expressed in degrees. The excellent agreement between theory and experiment is shown in Fig. 5.

For molecules with paramagnetism due entirely to spin the theory is simple, being in fact the same as that already applied in § 1414 to the ions of the transition elements. We then have

$$\mu_{eff}/\beta = 2\{S(S+1)\}^{\frac{1}{2}}. \tag{1417, 2}$$

* Van Vleck, p. 270.

The best established application of (2) is to $O_2$, which being in a $^3\Sigma$ state has $S = 1$. The susceptibility of oxygen at ordinary temperatures has been measured by numerous experimenters.* The observed effective magneton number is 2·84 in excellent agreement with the theoretical value $2\sqrt{2}$. The inverse proportionality between susceptibility and temperature, first found by P. Curie, has been confirmed with high accuracy by Kamerlingh Onnes and Oosterhuis,† whose data are shown in Fig. 6.

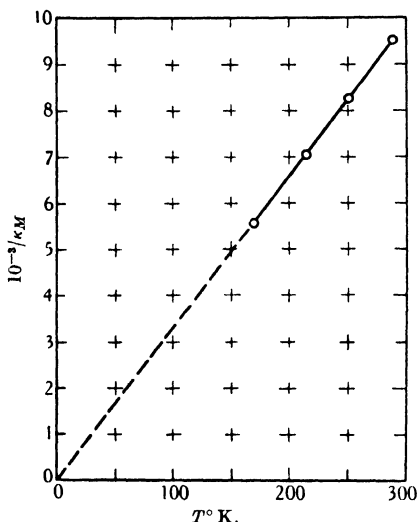



Fig. 6. Verification of Curie's law for gaseous oxygen by Kamerlingh Onnes and Oosterhuis. $\kappa_M$ denotes mass susceptibility (per gram).

The $NO_2$ molecule is definitely paramagnetic, but the determination of its molecular susceptibility is complicated by the simultaneous presence of $N_2O_4$ molecules. When a correction is applied for this, the value is in agreement‡ with that due to the spin of one odd electron. For $ClO_2$ dissolved in carbon tetrachloride the observed susceptibility is in fair agreement § with that due to the spin of one odd electron.

Finally we should mention that several odd organic molecules of the types $\begin{matrix} R \\ R' \end{matrix}\!\!>\!N\text{—}O$ and $R_2C\text{—}O\text{—}K$, where $R$, $R'$ denote organic radicals, have been studied by Sugden § and found to have a susceptibility corresponding to a spin of one odd electron.

* For details, see Stoner, p. 342.

† Kamerlingh Onnes and Oosterhuis, *Comm. Phys. Lab. Leiden*, no. 134*d*, 31 (1913).

‡ See Havens, *Phys. Rev.* **41**, 337 (1932).

§ For detailed references see Stoner, p. 477.

We have still to discuss the magnetic properties of metals, but, as this requires the use of Fermi-Dirac statistics, it is convenient to postpone doing so until after we have discussed electric susceptibilities, which we deal with next.

**§ 1418. Classical treatment of electric susceptibility for independent systems.** All molecules with a permanent electric moment, in contrast to ions with a permanent magnetic moment, are diatomic or polyatomic. Since even an approximate solution of Schrödinger's equation for the electronic structure of a molecule containing more than one atom is still out of question, we cannot calculate the Stark effect quantally for the actual molecule. We are therefore compelled to represent the molecule by a crude model to which we can apply either a classical or a quantal treatment. In the present section we shall give a classical treatment of two simple models. We assume that we may neglect interactions between the molecules, and shall later find that this assumption restricts the strict application of the formulae to perfect gases.

The classical treatment of electric susceptibility, which is closely analogous to Langevin's treatment of magnetic susceptibility, is due to Debye.* If we take as the model of the molecule a rigid dipole $\mu_0$, the classical treatment is the exact analogue of Langevin's described in § 1411. The partition function for this dipole in an external electric field $E$ will contain an orientational factor $O(T)$ given by

$$O(T) = \int_0^\pi e^{\mu_0 E \cos\theta/kT}\, 2\pi \sin\theta\, d\theta = 4\pi \frac{kT}{\mu_0 E} \sinh \frac{\mu_0 E}{kT}, \quad (1418, 1)$$

which is the electrical analogue of (1411, 1). The average component $\bar{\mu}$ of the moment along the field is given by the electrical analogue of (1411, 2)

$$\bar{\mu} = kT \frac{\partial \log O(T)}{\partial E} = \mu_0 L\left(\frac{\mu_0 E}{kT}\right), \quad (1418, 2)$$

where $L(\xi)$ is Langevin's function defined by (1411, 3). For the highest fields ordinarily used and for ordinary temperatures we can neglect powers of $E$ higher than the first, and replace (2) by

$$\bar{\mu} = \mu_0^2 E/3kT, \quad (1418, 3)$$

the electrical analogue of (1411, 5).

The model just discussed represents a molecule which can be orientated but is not polarized by the field. A more useful model for a molecule, which is polarizable as well as polar, is a dipole with an induced component $\gamma E$ parallel to the field in addition to a permanent orientatable component of

* Debye, *Phys. Zeit.* **13**, 97 (1912).

magnitude $\mu_0$. The two components are assumed to combine vectorially, the resultant component in the direction of the field being $\mu_0 \cos\theta + \gamma E$, where $\theta$ is the angle between $\mu_0$ and $E$. The corresponding mutual energy of the molecule and field is given by

$$\epsilon = -\mu_0 E \cos\theta - \tfrac{1}{2}\gamma E^2, \tag{1418, 4}$$

since the moment in the direction of the field is by definition equal to $-\partial\epsilon/\partial E$. We now obtain for the orientational factor $O(T)$ in the partition function

$$O(T) = \int_0^\pi e^{(\mu_0 E \cos\theta + \frac{1}{2}\gamma E^2)/kT}\, 2\pi \sin\theta\, d\theta$$
$$= 4\pi e^{\frac{1}{2}\gamma E^2/kT} \frac{kT}{\mu_0 E} \sinh \frac{\mu_0 E}{kT}. \tag{1418, 5}$$

The average component $\bar{\mu}$ of the moment along the field becomes

$$\bar{\mu} = kT \frac{\partial \log O(T)}{\partial E} = \mu_0 L\left(\frac{\mu_0 E}{kT}\right) + \gamma E, \tag{1418, 6}$$

or for ordinary fields at ordinary temperatures

$$\bar{\mu} = \left(\frac{1}{3}\frac{\mu_0^2}{kT} + \gamma\right) E. \tag{1418, 7}$$

For the electric susceptibility per molecule $\kappa_e$ we have therefore

$$\kappa_e = \frac{\bar{\mu}}{E} = \frac{1}{3}\frac{\mu_0^2}{kT} + \gamma, \tag{1418, 8}$$

which is Debye's formula for gases. His formula for liquids will be considered in §§ 1426–1427.

From (7) or (8) we see that the contribution to the susceptibility of the induced electric moment is independent of temperature and additive to the contribution of the permanent orientatable moment.

**§ 1419. Quantal justification.** The classical treatment of Debye requires a quantal justification. This was given by Van Vleck* by use of the principle of spectroscopic stability. We can hardly digress here sufficiently to give an adequate account of Van Vleck's proof, and must be content with a brief statement of his result. The proof applies equally to the electric and magnetic cases, but we shall state the result for the electric case.

In order that Debye's formula should hold for sufficiently large $T$, it is only necessary to assume that the molecule has a permanent electric dipole moment which is the same for a whole group of ("normal") states, with energy steps among themselves small compared with $kT$, and at the same

* Van Vleck, pp. 186–197 or *Phys. Rev.* **29**, 727 (1927).

time that this group of states is separated from all other ("excited") states by energy steps large compared with $kT$. These conditions are strictly complied with by most molecules at ordinary temperatures, the group of normal states being the various rotational states of the same normal electronic level. An exceptional type of molecule with a permanent moment which will not satisfy this condition is one with an internal rotation of a polar group such as $-OCH_3$.

**§ 1420. Simplest quantal model.** The reader who does not wish to study Van Vleck's treatment in full may still care to follow the details of the quantal treatment in the simplest case, that of a rigid rotator without axial spin having a permanent moment $\mu_0$ along its axis. In the absence of an external field the electric moment is irrelevant and the quantal states are those described in § 212. There are two quantum numbers $j$ and $m$ with the values

$$j = 0, 1, 2, \ldots, \qquad (1420, 1)$$

$$m = -j, -j+1, \ldots, j-1, j, \qquad (1420, 2)$$

and the energy values in the absence of a perturbing field are

$$\epsilon^0_{j,m} = \epsilon_j = j(j+1)\, h^2/8\pi^2 A, \qquad (1420, 3)$$

where $A$ is the transverse moment of inertia. Thus each $j$ level is degenerate with a weight $2j+1$. In an external field $E$ the degeneracy is removed and the splitting of the levels is the Stark effect. We can as usual express the levels in the presence of the field in the form

$$\epsilon_{j,m} = j(j+1)\, h^2/8\pi^2 A + a_{j,m} E + \tfrac{1}{2} b_{j,m} E^2, \qquad (1420, 4)$$

where the term $a_{j,m} E$ is the linear Stark effect and the term $\frac{1}{2} b_{j,m} E^2$ is the quadratic Stark effect; terms of higher order in $E$ are negligible. The coefficients $a_{j,m}$ and $b_{j,m}$ can be evaluated by the usual perturbation theory, the perturbation term in the Hamiltonian being $-\mu_0 E \cos\theta$.

It is found that

$$a_{j,m} = 0, \qquad (1420, 5)$$

so that there is no linear Stark effect for this model. This is in agreement with spectroscopic observation on the infra-red bands of HCl which show no linear Stark effect.

The coefficients of the quadratic Stark effect are found to be

$$b_{j,m} = -\frac{8\pi^2 A \mu_0^2}{h^2} \frac{3m^2 - j(j+1)}{j(j+1)(2j-1)(2j+3)} \quad (j \neq 0), \qquad (1420, 6)$$

$$b_{0,0} = -\frac{8\pi^2 A \mu_0^2}{h^2}. \qquad (1420, 7)$$

We can obtain the molecular susceptibility by substituting from (3), (5), (6) and (7) into (1403, 13). We require the sums $\sum_{m=-j}^{+j} b_{j,m}$. By using the identity

$$3\sum_{m=-j}^{+j} m^2 = j(j+1)(2j+1), \tag{1420, 8}$$

we deduce from (6) that

$$\sum_{m=-j}^{+j} b_{j,m} = 0 \quad (j \neq 0). \tag{1420, 9}$$

We thus have the striking result that not only is there no contribution from the $a_{j,m}^2$ terms, but the whole contribution of the $b_{j,m}$ terms comes from the single term $b_{0,0}$. Formula (1403, 13) therefore reduces to

$$\frac{\bar{\mu}}{E} = \frac{8\pi^2 A\mu_0^2}{3h^2}\Big/ r(T), \tag{1420, 10}$$

where $r(T)$ is the rotational partition function for zero field. At ordinary temperatures we can give $r(T)$ its classical value

$$r(T) = \frac{8\pi^2 A\,kT}{h^2}. \tag{1420, 11}$$

Substituting from (11) into (10), we obtain finally

$$\bar{\mu}/E = \mu_0^2/3kT, \tag{1420, 12}$$

thus confirming Debye's formula for this simple model.

According to Van Vleck's theorem any other suitable model, for example a symmetrical or an unsymmetrical top, will lead to Debye's formula for sufficiently high temperatures.

**§ 1421. Correlation of classical and quantal treatments.** The quantal treatment of the rigid rotator leads to the remarkable result that only molecules in the state $j = 0$, that is molecules with no rotation, contribute to the susceptibility. There was no indication of any analogous feature in the classical treatment given in § 1418, because we there completely ignored the rotational kinetic energy. This is allowable in a classical treatment. If, however, we include the kinetic energy in the classical treatment and group the molecules according to their total energy, kinetic and potential, it can be shown* that the resultant contribution of all the molecules with kinetic energy exceeding $\mu_0 E$ is zero, so that the whole contribution comes from those few molecules with kinetic energy less than $\mu_0 E$, which are those librating and not rotating in the field.

* Alexandrow, *Physikal. Zeit.* **22**, 258 (1921). Pauli, *Zeit. Phys.* **6**, 319 (1921).

The total energy $\epsilon$ is given by

$$\epsilon = \frac{1}{2A}\left(p_\theta^2 + \frac{p_\phi^2}{\sin^2\theta}\right) - \mu_0 E\cos\theta, \tag{1421, 1}$$

where $p_\theta$, $p_\phi$ are the momenta conjugate to the angle $\theta$ between the moment and the field and the azimuthal angle $\phi$ respectively. The average value of the component of the moment along the field is given by

$$\bar{\mu} = \frac{\int_0^\pi d\theta \int_0^{2\pi} d\phi \int_0^\infty dp_\theta \int_0^\infty dp_\phi\, \mu_0 \cos\theta e^{-\epsilon/kT}}{\int_0^\pi d\theta \int_0^{2\pi} d\phi \int_0^\infty dp_\theta \int_0^\infty dp_\phi\, e^{-\epsilon/kT}}. \tag{1421, 2}$$

We denote the total kinetic energy by $K$, define an angle $\beta$ by

$$\frac{1}{2A}p_\theta^2 = K\cos^2\beta, \quad \frac{p_\phi^2}{2A\sin^2\theta} = K\sin^2\beta, \tag{1421, 3}$$

and transform from the variables $p_\theta$, $p_\phi$ to the variables $K$, $\beta$. Then $dp_\theta dp_\phi$ transforms to

$$\begin{vmatrix} \partial p_\theta/\partial K & \partial p_\theta/\partial\beta \\ \partial p_\phi/\partial K & \partial p_\phi/\partial\beta \end{vmatrix} dK\,d\beta = A\sin\theta\, dK\,d\beta, \tag{1421, 4}$$

and (2) becomes

$$\bar{\mu} = \frac{\int_0^\pi d\theta \int_0^{2\pi} d\phi \int_0^\infty dK \int_0^{2\pi} d\beta\, \mu_0 \cos\theta\; A\sin\theta\, e^{-(K-\mu_0 E\cos\theta)/kT}}{\int_0^\pi d\theta \int_0^{2\pi} d\phi \int_0^\infty dK \int_0^{2\pi} d\beta\, A\sin\theta\, e^{-(K-\mu_0 E\cos\theta)/kT}}$$

$$= \frac{\int_0^\pi d\theta \int_0^\infty dK\, \mu_0\cos\theta\sin\theta\, e^{-(K-\mu_0 E\cos\theta)/kT}}{\int_0^\pi d\theta \int_0^\infty dK \sin\theta\, e^{-(K-\mu_0 E\cos\theta)/kT}}. \tag{1421, 5}$$

We now transform from the variables $\theta, K$ to the variables $\theta, \epsilon$. Since the kinetic energy cannot be negative, the lower range of integration for $\epsilon$ is $-\mu_0 E$ and the range of integration for $\theta$ will depend on $\epsilon$. As long as $\epsilon \geqslant \mu_0 E$ all values of $\theta$ from 0 to $\pi$ are allowable. But for $-\mu_0 E \leqslant \epsilon \leqslant \mu_0 E$ the range of values of $\theta$ is restricted by the condition $\epsilon + \mu_0 E\cos\theta \geqslant 0$. We have therefore

$$\bar{\mu} = \frac{\left\{\int_0^{\arccos(-\epsilon/\mu_0 E)} d\theta \int_{-\mu_0 E}^{\mu_0 E} d\epsilon + \int_0^\pi d\theta \int_{\mu_0 E}^\infty d\epsilon\right\} \mu_0\cos\theta\sin\theta\, e^{-\epsilon/kT}}{\left\{\int_0^{\arccos(-\epsilon/\mu_0 E)} d\theta \int_{-\mu_0 E}^{\mu_0 E} d\epsilon + \int_0^\pi d\theta \int_{\mu_0 E}^\infty dE\right\} \sin\theta\, e^{-\epsilon/kT}}. \tag{1421, 6}$$

Since $\int_0^\pi \cos\theta \sin\theta d\theta = 0$, the second term in the numerator vanishes and the whole contribution comes from the range of $\epsilon$ between $-\mu_0 E$ and $\mu_0 E$. The numerator thus reduces to

$$\int_0^{\arccos(-\epsilon/\mu_0 E)} d\theta \int_{-\mu_0 E}^{\mu_0 E} d\epsilon\, \mu_0 \cos\theta \sin\theta\, e^{-\epsilon/kT}$$

$$= \int_{-\mu_0 E}^{\mu_0 E} d\epsilon \frac{1}{2}\left(\frac{\epsilon}{\mu_0 E}\right)^2 \mu_0 e^{-\epsilon/kT} = \tfrac{1}{3}\mu_0^2 E, \qquad (1421,7)$$

when we neglect $\mu_0 E/kT$ compared with unity. To the same degree of accuracy the denominator reduces to

$$\int_0^\pi d\theta \int_0^\infty d\epsilon \sin\theta\, e^{-\epsilon/kT} = kT. \qquad (1421,8)$$

Inserting these values for the numerator and denominator of (6) we recover formula (1420, 2).

**§ 1422. Comparison of electric and magnetic susceptibilities.** In both electric and magnetic susceptibilities the temperature dependent term, which if present is usually the dominating one, is proportional to the square of the permanent moment. We have seen that permanent magnetic moments are of the order of magnitude of a Bohr magneton $\beta = |e|\, h/4\pi m_e c$. The order of magnitude of a permanent electric moment can be taken as the product of the magnitude of the charge of an electron $|e|$ and the radius of the Bohr orbit of a normal hydrogen atom $h^2/4\pi^2|e|^2 m_e$. We thus obtain for the order of magnitude of the ratio of molecular susceptibilities of the two types*

$$\frac{\kappa_e}{\kappa_m} \simeq \left(|e| \frac{h^2}{m_e|e|^2}\right)^2 \Big/ \left(\frac{|e|\, h}{m_e c}\right)^2 \simeq \left(\frac{hc}{2\pi|e|^2}\right)^2 = (137)^2. \qquad (1422,1)$$

Thus electric molecular susceptibilities are about $10^4$ times greater than magnetic molecular susceptibilities. For this reason the interaction between electric moments of different molecules cannot be neglected except in the dilute gaseous state, to which alone the formulae of the foregoing sections apply.

**§ 1423. Experimental data for gases.** It is implied in § 1424 that the dielectric constant $\delta$ of a gas of $N$ molecules in a volume $V$ is related to the electric molecular susceptibility $\kappa_e$ by

$$\delta = 1 + 4\pi \frac{N}{V} \kappa_e. \qquad (1423,1)$$

* This formula is taken from a lecture by Darwin.

Substituting from formula (1418, 8) into (1), we obtain Debye's formula

$$(\delta - 1)\,V = 4\pi\left(\frac{\mu_0^2}{3kT} + \gamma\right), \tag{1423, 2}$$

where $V = \mathsf{V}/N$ is the average volume per polar molecule. If then we plot $(\delta - 1)\,V$ against $1/T$, we should obtain straight lines. That this is borne out by experiment is shown by Fig. 7. In each case the slope of the straight line is according to (2) equal to $(4\pi/3k)\,\mu_0^2$. Table 3 shows the values of the electric moments thus determined for a variety of gases. The moments are usually given in Debye units of cm. × e.s.u. of charge × $10^{-18}$. The large moments found for $H_2O$ and $SO_2$ confirm the triangular model, while the zero value for $CO_2$ confirms the symmetrical linear structure.

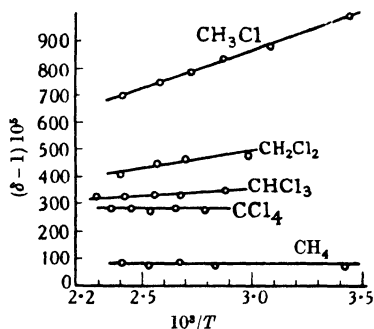



Fig. 7. Dependence on temperature of dielectric constants of gases and vapours. Experimental data of Sanger.

## TABLE 3

*Electric dipole moments of gaseous molecules calculated from Debye's equation*

The unit is the Debye unit = $10^{-18}$ e.s.u. cm.

| Gas | $\mu_0$ | Gas | $\mu_0$ | Gas | $\mu_0$ |
|---|---|---|---|---|---|
| HCl | 1·03 | $H_2O$ | 1·84 | $CH_4$ | 0·00 |
| HBr | 0·79 | $H_2S$ | 1·10 | $CH_3Cl$ | 1·89 |
| HI | 0·38 | $C_2H_2$ | 0·00 | $CH_2Cl_2$ | 1·59 |
| $NH_3$ | 1·48 | $C_2H_4$ | 0·00 | $CHCl_3$ | 0·95 |
| $PH_3$ | 0·55 | $C_2H_6$ | 0·00 | $CCl_4$ | 0·00 |
| $AsH_3$ | 0·15 | $N_2$ | 0·00 | NO | $>0$ |
| $SO_2$ | 1·61 | $CO_2$ | 0·00 | CO | 0·12 |

A summary of the best work to 1931 is given by Van Vleck, from whom most of the above values have been selected. An elaborate collection to 1934 is given by Sidgwick, *Trans. Far. Soc.* **30**, Appendix, p. i (1934).

**§ 1424. The electric field inside matter.** We have already mentioned that the foregoing treatment of electric moments applies only to gases. Before attempting to extend it to liquids, we must consider the rather complicated question of what we mean by the electric field inside matter.

For simplicity let us consider a parallel plate condenser filled with a homogeneous isotropic medium. Let the charge on unit area of the plates be $\pm\sigma$ and the distance between the plates be $l$. The electric potential difference between the plates is defined as the work per unit charge in transferring a small charge quasistatically from one plate to the other. This electric potential difference divided by $l$ is Maxwell's electric field $E$. Maxwell's electric displacement $D$ is defined as $4\pi\sigma$. From these definitions we see that $E$ has the dimensions of force/charge and $D$ has the dimensions charge/area. The product $ED$ thus has the dimensions of pressure or energy/volume. Suppose now the space between the plates to be empty. Then the laws of electrostatics tell us that the ratio $D/E$ is independent of $l$ and of $\sigma$ and is thus a universal constant, say $a$. The value of this universal constant clearly depends on the units.* If we use c.g.s. units for mass, length and time, we define the e.s.u. of charge by setting $a = 1$. On the other hand, the e.m.u. of charge is defined by setting $a = c^{-2}$, where $c$ is the velocity of light in c.g.s. units, that is in cm./sec. Thus in changing from e.s.u. to e.m.u. the magnitude of $D$ becomes multiplied by $c^{-1}$ and that of $E$ by $c$, the magnitude of $ED$ in ergs/cm.$^3$ thus remaining unaltered. This preamble is inserted to dispel the notion sometimes current that $E$ and $D$ have the same dimensions.

Let us return to the condenser filled with matter. We now define three kinds of electric field inside the matter. Firstly we imagine the matter removed from a small pipe-shaped cavity parallel to the field. We call the field in this cavity the pipe force and denote it by $E_p$. Secondly we imagine the matter removed from a narrow crack-shaped cavity across the field. We call the field in this cavity the crack force and denote it by $E_c$. Thirdly we imagine the matter removed from a small spherical cavity. We call the field in this cavity the sphere force and denote it by $E_s$. Then by elementary electrostatics it can be shown that

$$E_p = E, \qquad (1424, 1)$$

$$E_c = D/a, \qquad (1424, 2)$$

$$E_s = \tfrac{2}{3}E + \tfrac{1}{3}D/a. \qquad (1424, 3)$$

The measured dielectric constant $\delta$ is defined as the ratio of $D/E$ in the filled condenser to its value in the empty condenser. It follows that

$$\delta = D/aE. \qquad (1424, 4)$$

* Cf. Sommerfeld, *Zeit. Techn. Physik.* **16**, 420 (1935).

Using (4), we obtain in place of (1), (2) and (3)

$$E_p = E, \tag{1424, 5}$$

$$E_c = \delta E, \tag{1424, 6}$$

$$E_s = \tfrac{1}{3}(2+\delta)\,E. \tag{1424, 7}$$

Up to this point the exposition has been macroscopic and no reference has been or need be made to molecular structure. It can, however, be shown* that, if we regard the matter as consisting of point charges *in vacuo*, then the space-averaged field is $E$ or $E_p$. The average electric moment per unit volume in the direction of the field is $\bar{\mu}/V$, where $\bar{\mu}$ is the average component of the molecular moment in the direction of the field and $V$ is the molecular volume. This is related to the macroscopic field quantities by

$$4\pi\bar{\mu}/V = D - aE = a(E_c - E_p) = a(\delta - 1)\,E. \tag{1424, 8}$$

As long as we use electrostatic units we can replace $a$ throughout by unity and we shall do so just as we have done hitherto in previous paragraphs. If, however, any other units were used, we could not omit $a$ and it is for this reason that we have insisted on different symbols for $E_c$ and $D$, although in e.s.u. their values are equal. With this caution we replace (8) by

$$4\pi\bar{\mu}/V = E_c - E_p = (\delta - 1)\,E. \tag{1424, 9}$$

**§ 1425. Refractive index of gases and liquids.** According to the electromagnetic theory of light the refractive index $n$ and the dielectric constant $\delta$ are related by

$$n^2 = \delta. \tag{1425, 1}$$

For (1) to be accurate $n$ and $\delta$ must refer to electromagnetic waves of the same frequency. It is, however, customary to speak of the refractive index when referring to optical frequencies, and to speak of the dielectric constant when referring to much lower, including radio, frequencies. The dielectric constant $\delta$ for low frequencies is not necessarily equal to the square of the optical refractive index $n$. The reason is that at optical frequencies the molecules have not time to readjust their orientations as the field alternates. Thus only the induced moment makes a contribution to $n^2$. Corresponding to formula (1423, 2) for the dielectric constant of a gas, we have thus for its refractive index

$$(n^2 - 1)\,V = 4\pi\gamma. \tag{1425, 2}$$

For a gas with non-polar molecules the equality (1) should hold even when $n$ refers to an optical frequency and $\delta$ to a low frequency. For a gas with polar molecules the dielectric constant should always exceed the square of the refractive index owing to the positive orientational term. These theoretical predictions are completely borne out by experiment.

* Lorentz, *The Theory of Electrons* (Teubner, 1909); Darwin, *Proc. Roy. Soc.* A, **146**, 17 (1934).

We turn now to consider liquids. The electron theory of the refractive index is due to Lorentz. The fundamental assumption of Lorentz' theory* is that the field acting on an individual molecule is the sphere force $E_s$. We postpone for the moment any attempt to justify this assumption and we proceed to examine its consequences. We have now to modify formula (1418, 7) for $\bar{\mu}$, the average component of the electric moment in the direction of the field, in two respects. We have to omit the orientational term containing $\mu_0^2$, because we are considering optical frequencies, and, accepting Lorentz' assumption, we have to replace $E$ by $E_s$. We have then

$$\bar{\mu} = \gamma E_s. \qquad (1425, 3)$$

We also have according to (1424, 7)

$$E_s = \tfrac{1}{3}(2+n^2)\,E, \qquad (1425, 4)$$

and according to (1424, 9)

$$4\pi\bar{\mu}/V = (n^2-1)\,E. \qquad (1425, 5)$$

If we eliminate $\bar{\mu}$ and $E_s$ from (3), (4) and (5), we obtain

$$\gamma = \frac{3}{4\pi}\frac{n^2-1}{n^2+2}V. \qquad (1425, 6)$$

From observed values of the refractive index $n$ and molecular volume $V$ we can compute the right-hand side of (6); this should be equal to the molecular polarizability $\gamma$, a molecular constant independent of temperature and pressure. It is customary to multiply both sides of (6) by Avogadro's number $\mathsf{N}$ for obvious reasons, and also by $4\pi/3$ for no clear reason. One thus obtains the Lorenz-Lorentz formula†

$$\frac{4\pi}{3}\mathsf{N}\gamma = \frac{n^2-1}{n^2+2}\mathsf{N}V. \qquad (1425, 7)$$

The right-hand side of (7) is called the *molar optical polarization*, an established but unfortunate name, since the optical polarizability per mole is $\mathsf{N}\gamma$, or $3/4\pi$ times the optical molar polarization.

A first test of Lorentz' assumption is whether the right side of (7) is independent of temperature and pressure. In the gaseous state, or over the small range of variation of $V$ in the liquid state, the right side of (7) is in fact found to remain almost constant, but not much more accurately than $(n^2-1)\mathsf{N}V$ or various other empirical expressions. The crucial test of Lorentz' assumption is whether the molar optical polarization has the same value in the liquid as in the gas. This equality has been confirmed to within 1 part in 4000 for $N_2$, and to within 3 parts in 1000 for $O_2$. Even for such an abnormal liquid as water the value of the molar optical polarization is only

* See Lorentz, *The Theory of Electrons*, p. 138 (Teubner, 1909).

† Cf. Lorentz, *The Theory of Electrons*, p. 145 (Teubner, 1909).

10% different from the value in the vapour, although the molar volume $\mathbf{N}V$ changes by a factor of $10^3$.

We have now to consider the justification of Lorentz' assumption that the field acting on each molecule is the sphere force $E_s$ defined as the value of $E$ in a small spherical cavity. The choice of a spherical cavity rather than some other shape is dictated by the need of simplicity. If the molecule were spherical, it would moreover be the obvious choice. Even if the molecule is not spherical, it is presumably rotating, and a sphere is perhaps not a bad approximation to the volume around it which is excluded for other molecules. Moreover, if one tried to use a cavity of shape resembling that of the molecule, this cavity could be orientated in all directions and the average force for all orientations of the cavity would probably be nearly the same as the force in a spherical cavity. A much more serious objection to Lorentz' assumption is that the average force in a cavity placed at random is not obviously equal to the average force in an imaginary cavity placed at the spot occupied by a molecule. Quite recently Van Vleck* has shown that in quantum theory, Lorentz' assumption would be accurate if the polarizable particles were harmonic oscillators arranged on a regular lattice with cubic symmetry. It is satisfactory that Lorentz' assumption has now been shown to be rigorous for just the very model that Lorentz was using. We may therefore expect the Lorenz-Lorentz formula for the molecular polarizability $\gamma$ to be the more nearly accurate, the more nearly this polarizability resembles that of a harmonic oscillator.

**§ 1426. Dielectric constants of liquids.** We turn next to the low frequency dielectric constants of liquids. There is now an important difference between liquids with polar and those with non-polar molecules. For liquids with non-polar molecules the low frequency dielectric constant is equal to the square of the optical refractive index $n$. Corresponding to formula (1425, 6) we have

$$\gamma = \frac{3}{4\pi}\frac{\delta - 1}{\delta + 2}V. \qquad (1426, 1)$$

It is again customary to multiply both sides not by $\mathbf{N}$ but by $\frac{4}{3}\pi\mathbf{N}$. We thus obtain the Clausius-Mosotti relation

$$\tfrac{4}{3}\pi\mathbf{N}\gamma = \frac{\delta - 1}{\delta + 2}\mathbf{N}V. \qquad (1426, 2)$$

The right side, a purely experimental quantity, is called the *molar total polarization*. For non-polar liquids it is found to have a value independent of temperature, equal to its value for the gas and to the molar optical polarization.

* Van Vleck, *J. Chem. Phys.* **5**, 565 (1937); cf. Darwin, *Proc. Roy. Soc.* A, **146**, 17 (1934).

For liquids with polar molecules, if we tentatively continue to assume that the electric field acting on a molecule is $E_s$, we have instead of formula (1418, 7)

$$\bar{\mu} = (\mu_0^2/3kT + \gamma)\, E_s \qquad (1426, 3)$$

Eliminating $E_s$ and $\bar{\mu}$ from (3), (1424, 7) and (1424, 9), we obtain

$$\frac{\mu_0^2}{3kT} + \gamma = \frac{3}{4\pi}\frac{\delta - 1}{\delta + 2} V, \qquad (1426, 4)$$

or on multiplication by $\frac{4}{3}\pi \mathsf{N}$

$$\tfrac{4}{3}\pi \mathsf{N}\left(\frac{\mu_0^2}{3kT} + \gamma\right) = \frac{\delta - 1}{\delta + 2} \mathsf{N} V. \qquad (1426, 5)$$

Finally, subtracting (1425, 7) from (5), we find

$$\tfrac{4}{3}\pi \mathsf{N} \frac{\mu_0^2}{3kT} = \frac{\delta - 1}{\delta + 2} \mathsf{N} V - \frac{n^2 - 1}{n^2 + 2} \mathsf{N} V, \qquad (1426, 6)$$

a formula due to Debye. The right side of (6), which is the difference between the molar total polarization and the molar optical polarization, is called the *molar orientational polarization*. It is a purely experimental quantity from which, subject to the assumption made, we can calculate $\mu_0$ by means of (6).

It has never been seriously suggested that one can calculate reliable molecular moments by applying (6) to pure polar liquids, because it is realized that in polar liquids there is almost always some kind of "association" in the most general sense of the word. Whether or not the "association" consists in the formation of multiple molecules, it is unlikely that the molecules are sufficiently free to orientate independently of one another.

Formula (6) is easily generalized for a mixture of two or more liquids, and the usual practice for determining electric moments in the liquid state is to use the extended form of (6) for a dilute solution of a polar substance in a non-polar solvent. Since there exists an extensive literature concerning* the application of this method of estimating electric moments we shall not devote any space to details, but shall rather confine ourselves to a critical discussion of the underlying assumption, namely that the electric field acting on a molecule may be taken to be $E_s$.

**§ 1427. Inadequacy of Debye's formula.** For a critical discussion of Debye's formula (1426, 6) it is convenient to introduce a characteristic temperature $\Theta_0$, defined by

$$k\Theta_0 = \frac{4\pi}{9}\frac{\mu_0^2}{V}, \qquad (1427, 1)$$

* See for example Debye, *Polar Molecules* (New York, 1929), and also Discussion by Faraday Society, *Trans. Far. Soc.* **30**, 677 (1934).

where $\mu_0$ is the molecular electric dipole moment and $V$ is the molecular volume in the liquid. For computational purposes it is convenient to rewrite (1) in the form

$$\Theta_0 = \frac{(\mu_0 \text{ in Debye units}/1{\cdot}27 \times 10^{-2})^2}{\text{molar volume in cm.}^3}. \qquad (1427, 2)$$

The following are some typical values of $\Theta_0$:

$HBr$: $\Theta_0 = 120°$. $HCl$: $\Theta_0 = 260°$.

$H_2O$: $\Theta_0 = 1200°$. $C_6H_5NO_2$: $\Theta_0 = 1100°$.

Debye's formula (1426, 6) can be written in the form

$$\frac{\Theta_0}{T} = \frac{\delta-1}{\delta+2} - \frac{n^2-1}{n^2+2} = \frac{3(\delta-n^2)}{(\delta+2)(n^2+2)}. \qquad (1427, 3)$$

If we define another temperature $\Theta_c$ by

$$\Theta_c = \tfrac{1}{3}(n^2+2)\,\Theta_0, \qquad (1427, 4)$$

we note that the ratio $\Theta_c/\Theta_0$ will never be very different from unity, and we can now rewrite (3) in the alternative form

$$\frac{\delta-1}{\delta+2} = \frac{n^2-1+3(\Theta_c/T)}{n^2+2}. \qquad (1427, 5)$$

According to (5) we can have finite positive values of $\delta$ only when $T > \Theta_c$. When $T = \Theta_c$ formula (5) reduces to

$$\frac{\delta-1}{\delta+2} = 1, \quad \delta = \infty. \qquad (1427, 6)$$

This implies the persistence of an electric moment in the absence of an electric field, an electrical analogue of ferromagnetism. Such a phenomenon is possible, but we can safely say that it does not occur as a rule in liquids at any temperature $\Theta_c$ of the order of magnitude of the $\Theta_0$ values mentioned above. We conclude that Debye's formula, if applied to pure liquids, is in direct contradiction with experiment. One might argue that the non-occurrence of permanent electric polarization is due to association of polar molecules to form non-polar (or less polar) complexes. It is true that the greater the polarity of a molecule the more likely it is to associate with other molecules, but, as we mentioned in § 800, the extent and nature of association depend very much on the shape of a molecule and on where the electric moment is situated. A liquid such as chloroform, consisting of molecules with a dipole moment by no means negligible but situated more or less in the middle of the molecule, behaves as a normal rather than an associated liquid. It would be more satisfactory if one could explain the usual absence of an electric analogue of ferromagnetism without the need

of invoking association. It has been shown by Onsager* that this is in fact possible without making any *ad hoc* assumptions. We shall now summarize Onsager's treatment and the conclusions to which it leads.

**§ 1428. Onsager's improvement on Debye's formula.** The weakness in Debye's treatment is that it assumes that the field acting on a given polar molecule is always $E_s$, which is parallel to the applied field and is independent of the instantaneous orientation of the given molecule. This defect is removed by Onsager, who uses the simplest possible electrostatic model. Following Onsager, we regard a molecule as a sphere of radius $a$, with a polarizability $\gamma$ related to a refractive index $n$ by the Lorenz-Lorentz formula (1425, 6), which we can write in the form

$$\gamma = \frac{n^2-1}{n^2+2}a^3. \qquad (1428,1)$$

We have already referred to Van Vleck's justification of this formula in so far as the polarizability can be represented as due to harmonic oscillations. We further suppose that a molecule isolated in free space has a permanent electric moment $\mu_0$. We now suppose this spherical molecule to be immersed in a continuous medium of dielectric constant $\delta$, in a homogeneous electric field $E$. Eventually this medium is to represent the smoothed effect of molecules exactly similar to the particular molecule under consideration, which we may call the central molecule. We now use Clarendon type to refer to vectors. By straightforward electrostatics it can be shown that for a given orientation of the central molecule the electric force $\mathbf{F}$ acting on it is given by

$$\mathbf{F} = \frac{3\delta}{2\delta+1}\mathbf{E} + \frac{2(\delta-1)}{(2\delta+1)a^3}\boldsymbol{\mu}. \qquad (1428,2)$$

Using (1) we can rewrite this as

$$\mathbf{F} = \frac{3\delta}{2\delta+1}\mathbf{E} + \frac{2(\delta-1)}{(2\delta+1)\gamma}\frac{n^2-1}{n^2+2}\boldsymbol{\mu}. \qquad (1428,3)$$

If we denote by $\mathbf{u}$ the unit vector in the direction of the (instantaneous) orientation of the dipole $\mu_0$, we have by definition

$$\boldsymbol{\mu} = \mu_0\mathbf{u} + \gamma\mathbf{F}. \qquad (1428,4)$$

Eliminating $\mathbf{F}$ from (3) and (4), we obtain

$$\begin{aligned}\boldsymbol{\mu} &= \frac{(n^2+2)(2\delta+1)}{3(2\delta+n^2)}\mu_0\mathbf{u} + \frac{\delta(n^2+2)}{2\delta+n^2}\gamma\mathbf{E} \\ &= \frac{(n^2+2)(2\delta+1)}{3(2\delta+n^2)}\mu_0\mathbf{u} + \frac{\delta(n^2-1)}{2\delta+n^2}a^3\mathbf{E}, \qquad (1428,5)\end{aligned}$$

* Onsager, *J. Am. Chem. Soc.* **58**, 1486 (1936).

using (1). The (instantaneous) couple acting on the central molecule is

$$\mathbf{F} \times \boldsymbol{\mu} = \frac{3\delta}{2\delta+1} \mathbf{E} \times \boldsymbol{\mu}. \qquad (1428, 6)$$

In deriving (6) we have used (3) and the identity $\boldsymbol{\mu} \times \boldsymbol{\mu} = 0$. If we now substitute from (5) into (6) and use the identity $\mathbf{E} \times \mathbf{E} = 0$, we obtain for the couple acting on the central molecule

$$\frac{\delta(n^2+2)}{2\delta+n^2} \mu_0 \mathbf{E} \times \mathbf{u}. \qquad (1428, 7)$$

This is a couple at right angles to the instantaneous direction of $\mu_0$ and of magnitude

$$\frac{\delta(n^2+2)}{2\delta+n^2} \mu_0 E \sin\theta, \qquad (1428, 9)$$

where $\theta$ denotes the angle between $\mathbf{u}$ and $\mathbf{E}$. The corresponding (instantaneous) orientational energy $\epsilon$ is, apart from an arbitrary constant, given by

$$\epsilon = -\frac{\delta(n^2+2)}{2\delta+n^2} \mu_0 E \cos\theta. \qquad (1428, 10)$$

The average (equilibrium) value of $\cos\theta$ is determined by the usual statistical formula

$$\overline{\cos\theta} = \frac{\int_0^\pi \cos\theta\, e^{-\epsilon/kT} \sin\theta\, d\theta}{\int_0^\pi e^{-\epsilon/kT} \sin\theta\, d\theta}. \qquad (1428, 11)$$

Inserting the value of $\epsilon$ given by (10) into (11) and performing the integrations, we obtain

$$\overline{\cos\theta} = \frac{\delta(n^2+2)}{2\delta+n^2} \frac{\mu_0 E}{3kT}. \qquad (1428, 12)$$

The instantaneous component of the moment along the field $\mathbf{E}$ is obtained by replacing $\mathbf{u}$ by $\cos\theta$ and $\mathbf{E}$ by $E$ in (5). To obtain the average (equilibrium) value of the dipole moment along the field we have merely to replace $\cos\theta$ by $\overline{\cos\theta}$ given by (12). We thus find

$$\bar{\mu} = \frac{(n^2+2)(2\delta+1)}{3(2\delta+n^2)} \frac{\delta(n^2+2)}{2\delta+n^2} \frac{\mu_0^2 E}{3kT} + \frac{\delta(n^2-1)}{2\delta+n^2} a^3 E. \qquad (1428, 13)$$

We now assume that this formula determines the average component of moment along the field not merely of a special central molecule, but of all the molecules in the liquid. We then have, by definition of the dielectric constant,

$$\delta - 1 = \frac{4\pi}{V} \frac{\bar{\mu}}{E}, \qquad (1428, 14)$$

where $V$ is the molecular volume. Eliminating $\bar{\mu}$ from (13) and (14), we obtain

$$\delta - 1 = \frac{4\pi}{V} \frac{(n^2+2)(2\delta+1)}{3(2\delta+n^2)} \frac{\delta(n^2+2)}{2\delta+n^2} \frac{\mu_0^2}{3kT} + \left(\frac{4\pi}{3}\frac{a^3}{V}\right) \frac{3\delta(n^2-1)}{2\delta+n^2}. \quad (1428, 15)$$

To proceed further we have to decide what value to assign to the molecular radius $a$. Onsager takes $a$ to be the radius of a sphere of volume equal to the molecular volume so that

$$\tfrac{4}{3}\pi a^3 = V. \quad (1428, 16)$$

This assumption seems arbitrary, but we may accept it for the purpose of a semi-quantitative investigation of formula (15). Using (16) we find that (15) reduces to

$$\frac{4\pi}{3V} \frac{\mu_0^2}{3kT} = \frac{(\delta-n^2)(2\delta+n^2)}{\delta(n^2+2)^2} \quad \text{(Onsager)}. \quad (1428, 17)$$

For convenience of comparison with (17) we write Debye's formula (1426, 6) in the form

$$\frac{4\pi}{3V} \frac{\mu_0^2}{3kT} = \frac{3(\delta-n^2)}{(\delta+2)(n^2+2)} \quad \text{(Debye)}. \quad (1428, 18)$$

According to (17) in contrast with (18) we observe that $\delta$ never becomes infinite except when $T$ is zero. The quantitative usefulness of (17) is decreased by the inexactness of (16), and by uncertainty concerning the extent, nature and effect of association. The important achievement of Onsager's treatment is rather the proof that, even in the absence of any kind of association, an electrical analogue of ferromagnetism need not occur at ordinary temperatures, as in fact it does not.

In the trivial case $\delta = n^2$, corresponding to non-polar molecules, formulae (17) and (18) agree, but whenever $\delta > n^2$, as must be the case for polar molecules, the right side of (17) is always greater than the right side of (18). For any given $n^2$ the ratio departs further from unity as $\delta$ increases.

It is of some interest to contrast the predictions of formulae (17) and (18) for highly polar liquids, that is to say liquids with high dielectric constants. For the purpose of rough comparison we suppose that $n^2 \simeq 2$, a reasonable average value for liquids. Debye's formula (18) becomes

$$\frac{4\pi}{3V} \frac{\mu_0^2}{3kT} = \frac{3}{4}\left\{1 - \frac{4}{\delta} + O\frac{1}{\delta^2}\right\} \simeq \frac{3}{4}\left(1 - \frac{4}{\delta}\right), \quad (1428, 19)$$

whereas Onsager's formula (17) reduces to

$$\frac{4\pi}{3V} \frac{\mu_0^2}{3kT} = \frac{\delta}{8}\left\{1 - \frac{1}{\delta} - \frac{2}{\delta^2}\right\} \simeq \frac{\delta}{8}. \quad (1428, 20)$$

The left side of (19) or (20) can be calculated from values of $\mu_0$ obtained either from measurements on the vapour or, with sufficient accuracy, from measurements made on dilute solutions in a non-polar solvent. Using these

values of $\mu_0$ and the experimental values of $\delta$ for pure polar liquids, one can compare formulae (19) and (20) with experiment. It is found that, if one excludes water, alcohols and ammonia, i.e. typical associated liquids, while there is no agreement whatever with (19), there is a quite remarkable, albeit very rough, agreement* with (20).

**§ 1429. Comparison of Onsager's and Van Vleck's formulae.** It is of interest to compare Onsager's formula with a formula obtained by Van Vleck by an entirely different method. For the sake of simplicity and brevity we shall confine ourselves to the case when $(n^2-1)/(\delta-1) \ll 1$, a condition roughly fulfilled for small molecules with a large electric moment. We accordingly replace $n^2$ by 1; the distinction between the characteristic temperatures $\Theta_c$ and $\Theta_0$ now disappears, and we accordingly write simply $\Theta$. Formula (1428, 17) can now be written

$$\frac{(\delta-1)(2\delta+1)}{9\delta} = \frac{\Theta}{T} \qquad \text{(Onsager).} \qquad (1429, 1)$$

This is a quadratic in $\delta$ with the relevant root

$$\delta - 1 = \frac{3}{4}\left\{\left(1+\frac{2\Theta}{T}+\frac{9\Theta^2}{T^2}\right)^{\frac{1}{2}} - 1 + \frac{3\Theta}{T}\right\}. \qquad (1429, 2)$$

If we expand in powers of $\Theta/T$, we obtain

$$\delta - 1 = 3\frac{\Theta}{T}\left\{1+\frac{\Theta}{T}-\frac{\Theta^2}{T^2}-\frac{\Theta^3}{T^3}+O\left(\frac{\Theta^4}{T^4}\right)\right\}, \qquad (1429, 3)$$

but we would emphasize that the condition for the convergence of this expansion is

$$\frac{\Theta}{T} < \frac{\sqrt{10}-1}{9} = 0{\cdot}24. \qquad (1429, 4)$$

Van Vleck has also obtained an expression for $\delta - 1$ as a power series in $\Theta/T$. We shall not describe the method here, because it is the same method as applied to an analogous magnetic problem in § 1435, where the method is briefly described. If we continue to neglect the distinction between $\Theta_0$ and $\Theta_c$, Van Vleck's† formula may be written

$$\delta - 1 = 3\frac{\Theta}{T}\left\{1+\frac{\Theta}{T}+\left[1-Q\left(\frac{3}{4\pi}\right)^2\right]\frac{\Theta^2}{T^2}+O\left(\frac{\Theta^3}{T^3}\right)\right\}. \qquad (1429, 5)$$

Here $Q$ is defined by $$Q = 2V^2\Sigma_j r_{ij}^{-6}, \qquad (1429, 6)$$

where $V$ is the molecular volume and $r_{ij}$ is the distance from any selected molecule $i$ to any molecule $j$ other than $i$ itself. $Q$ is a pure number, whose

* Cf. Wyman, *J. Am. Chem. Soc.* **58**, 1482 (1936).
† Van Vleck, *J. Chem. Phys.* **5**, 556 (1937).

value depends on the manner of packing of the molecules. For simple cubic packing $Q = 16{\cdot}8$, for face-centred cubic packing $Q = 14{\cdot}4$, and for body-centred cubic packing $Q = 14{\cdot}5$. To compare formula (5) with Onsager's formula we have to replace $Q$ by an analogous quantity for a continuum, and so assume

$$Q = 2\frac{4\pi a^3}{3}\int_a^\infty r^{-6}4\pi r^2\,dr = 2\left(\frac{4\pi}{3}\right)^2 = 35{\cdot}1. \qquad (1429,7)$$

When we substitute this value of $Q$ into (5), we obtain

$$\delta - 1 = 3\frac{\Theta}{T}\left\{1 + \frac{\Theta}{T} - \frac{\Theta^2}{T^2} + O\left(\frac{\Theta^3}{T^3}\right)\right\}, \qquad (1429,8)$$

which agrees with Onsager's formula (3) up to the highest term evaluated. This agreement is particularly satisfactory, since formulae (3) and (5) were derived by entirely different procedures. The agreement is maintained when the induced moments are not neglected, as they have been here by replacing $n^2$ by 1. The analogous form of Debye's formula (1428, 18), when $n^2$ is replaced by unity, is

$$\delta - 1 = \frac{3\Theta}{T-\Theta} = 3\frac{\Theta}{T}\left\{1 + \frac{\Theta}{T} + \frac{\Theta^2}{T^2} + \ldots\right\}, \qquad (1429,9)$$

which disagrees with Onsager's formula in the third term.

Van Vleck does not investigate the condition for the convergence of his series. There is no reason to suppose that the condition is any less severe than (4). The series is therefore likely to be completely unreliable when $T/\Theta$ approaches unity. We therefore omit any further discussion of these series.

From Onsager's treatment we conclude that, quite apart from association, Debye's formula is not accurate for liquids. There is no reason to suppose that the analogous formula for solutions is any more accurate. Values of electric moments obtained by the application of this formula to solutions are therefore likely to be only approximate. A detailed extension of Onsager's treatment to solutions would be interesting. Onsager indicates very briefly how this might be done, but the method has not been developed in detail.

**§ 1430. Refractive index and dielectric constant of imperfect gases.** We mentioned in § 1425 that Van Vleck has shown that the Lorenz-Lorentz formula

$$\frac{n^2-1}{n^2+2}V = \frac{4\pi}{3}\gamma \qquad (1430,1)$$

is accurate for a non-polar solid or liquid in so far as the polarizable molecules may be regarded as harmonic oscillators. It might be expected that this would be true *a fortiori* for an imperfect gas, but such is not the case. For the derivation of (1) is based on the assumption of a regular spacing of the molecules, a condition holding accurately in a crystal and with fair accuracy

even in a liquid. In a gas on the other hand, owing to the large fluctuations in the distances between pairs of nearest molecules, the mean inverse sixth power of the distance of separation is not at all the same as the square of the mean inverse cube. This has the effect, called the translational fluctuation effect, of causing deviations from (1), so that we have instead a relation of the form

$$\frac{n^2-1}{n^2+2}V = \frac{4\pi}{3}\gamma\left\{1+\lambda\frac{4\pi\gamma}{3V}+O\left(\frac{\gamma}{V}\right)^2\right\}. \qquad (1430, 2)$$

The coefficient $\lambda$ has been calculated by Van Vleck* for spherical molecules with diameter $D$, polarizability $\gamma$ and mutual interactions corresponding to quantal harmonic oscillators of frequency $\nu$. He finds for $\lambda$ the formula

$$\lambda = \frac{2\gamma}{D^3}\left\{1+\frac{1}{2}\frac{\gamma}{D^3}+\frac{\gamma^2}{D^6}\left(1+\frac{1}{4}\frac{h\nu}{kT}\right)+\dots\right\}. \qquad (1430, 3)$$

If the second virial coefficient $B$ of an imperfect gas is written in the approximate form

$$B = \frac{2\pi}{3}D^3 - \frac{a}{kT}, \qquad (1430, 4)$$

corresponding to Van der Waals' equation, then $a$ is given by

$$a = \frac{\pi h\nu\gamma^2}{2D^3}. \qquad (1430, 5)$$

We can therefore write (3) in the alternative form

$$\lambda = \frac{2\gamma}{D^3}\left\{1+\frac{1}{2}\frac{\gamma}{D^3}+\frac{\gamma^2}{D^6}+\frac{a}{2\pi D^3kT}+\text{smaller terms}\right\}. \qquad (1430, 6)$$

For gases such as $H_2$, $N_2$, $O_2$ the value $\gamma/D^3 \simeq 0{\cdot}05$, whereas $a/2\pi D^3kT \simeq 0{\cdot}5$ at ordinary temperatures. One may therefore without serious error replace (6) by the approximation

$$\lambda = \frac{2\gamma}{D^3}\left\{1+\frac{a}{2\pi D^3kT}+\text{smaller terms}\right\}, \qquad (1430, 7)$$

a formula previously obtained by Kirkwood.†

The calculated values of $\lambda$ for $H_2$, $N_2$, $O_2$ at 0° C. are about 0·12 and the deviations from (1) are within the experimental error. A deviation of this type has been confirmed by recent measurements‡ on carbon dioxide and propane.

For non-polar imperfect gases there is no need to distinguish between $n^2$ and $\delta$. For imperfect gases with polar molecules the two quantities are distinct, and there is a formula analogous to (2) for the dielectric constant.

* Van Vleck, *J. Chem. Phys.* **5**, 991 (1937). † Kirkwood, *J. Chem. Phys.* **4**, 592 (1936).
‡ Keyes and Oncley, *Chem. Rev.* **19**, 195 (1936).

A formula for the coefficient analogous to $\lambda$ has been obtained by Van Vleck,* but we shall not consider it here.

**§ 1431. Entropy of paramagnetic salts.** We now return to the subject of magnetism, to discuss the properties of salts containing a paramagnetic ion at very low temperatures, that is to say temperatures below 10° K., and particularly temperatures between 1° K. and 0·01° K. For the purpose of this discussion we assume that the paramagnetic ions either are in S states like $Gd^{+++}$ and $Fe^{+++}$, or are at least effectively in S states like $Ti^{+++}$ and $Cr^{+++}$, owing to complete quenching of the orbital angular momentum as described in § 1415. The orientational electronic partition function $e(H, T)$ for an ion in an S state, or in an effective S state, in a magnetic field $H$ is, as we saw in § 1416,

$$e(H,T) = \frac{\sinh\{(2S+1)\beta H/kT\}}{\sinh\{\beta H/kT\}}. \qquad (1431,1)$$

Since we shall be particularly interested in reversible adiabatic changes, i.e. processes at constant entropy, we shall require formulae for the entropy. The orientational electronic contribution to the entropy of an assembly is due to the orientation of the resultant electronic spins of the paramagnetic ions and we shall denote it by $S^{\text{sp}}$. It is given by

$$\frac{S^{\text{sp}}}{Nk} = \frac{\partial}{\partial T}\{T\log e(H,T)\}. \qquad (1431,2)$$

For the sake of brevity we introduce a dimensionless quantity $x$ defined by

$$x = \beta H/kT. \qquad (1431,3)$$

Substituting from (1) into (2) and using the abbreviation (3), we obtain†

$$\frac{S^{\text{sp}}}{Nk} = \log\frac{\sinh\{(2S+1)x\}}{\sinh x} - (2S+1)x\coth\{(2S+1)x\} + x\coth x. \quad (1431,4)$$

At temperatures below 10° K. we may safely assume the validity of Debye's limiting law for the acoustical modes, so that their contribution $S^{\text{ac}}$ to the entropy is of the form

$$\frac{S^{\text{ac}}}{Nk} = a\frac{T^3}{\Theta_D^3} \quad (a \text{ a pure number}). \qquad (1431,5)$$

In the temperature range below 10° K. we have then for a reversible adiabatic process

$$S^{\text{sp}} + S^{\text{ac}} = \text{const.}, \qquad (1431,6)$$

since all other contributions to the entropy are either zero (e.g. rotations

* Van Vleck, *J. Chem. Phys.* **5**, 991 (1937).

† There can be no fear of confusing the quantum number $S$ with the entropy $S$.

and internal vibrations of molecules or ions), or independent of the temperature (e.g. nuclear spin and other nuclear internal degrees of freedom).

When $x \ll 1$ (sufficiently small $H$), formula (4) takes the limiting form

$$\frac{S^{\mathrm{sp}}}{Nk} = \log(2S+1) - \frac{1}{6}\frac{4S(S+1)\beta^2 H^2}{k^2 T^2} \quad (x = \beta H/kT \ll 1). \quad (1431, 7)$$

In particular we have in the absence of a magnetic field

$$S^{\mathrm{sp}}/Nk = \log(2S+1) \quad (H = 0), \quad (1431, 8)$$

an obvious result, since $2S+1$ is simply $\varpi_0$, the electronic weight of the ground electronic state.

When $x \gg 1$ (sufficiently small $T$ with finite $H$), formula (4) becomes

$$S^{\mathrm{sp}} = 0. \quad (1431, 9)$$

The physical significance of (9) is that all the ions are parallel to the field and there is magnetic saturation.

It is important to note that when $H$ and $T$ are varied simultaneously in a constant ratio so as to keep $x$ constant, the value of $S^{\mathrm{sp}}$ remains unaltered.

**§ 1432. Cooling by adiabatic demagnetization.** Although the production of low temperatures may require great experimental skill and resources; the theoretical principle involved is extremely simple.* Let us suppose that the state of an assembly is defined by the temperature and one or more other parameters $\xi_1, \xi_2, \ldots$, so that in particular the entropy $S$ is of the form

$$S = S(T, \xi_1, \xi_2, \ldots). \quad (1432, 1)$$

Provided one of the quantities $\xi_1, \xi_2, \ldots$, say $\xi_1$, can be *controlled and varied reversibly*, then evidently, by varying $\xi_1$ under reversible adiabatic conditions, one can obtain either a rise or fall of $T$ according to the direction of the change in $\xi_1$. From a practical point of view the important question is whether there is a suitable $\xi_1$ which will produce a sufficiently great change of $T$ to make the process worth while. We shall now explain why the choice of a magnetic field $H$ as the variable $\xi_1$ is a particularly useful one at low temperatures, and provides an efficient means of covering the temperature range with an upper end between 4° K. and 0·1° K. and a lower end between 0·01° K. and 0·001° K. This method of attaining such low temperatures was proposed almost simultaneously† by Giauque and by Debye.

In an assembly whose state can be completely defined by the temperature $T$ and the magnetic field $H$ (all other degrees of freedom such as the pressure

* Cf. Simon, "Very Low Temperatures", *Science Museum Handbook*, no. 3, p. 58 (1937).

† An interesting account of the history of the subject and the results obtained is given by Giauque, *Proc. 7th Int. Cong. Refrigeration* (1936).

and composition being either irrelevant or held constant), the equation for a reversible adiabatic process has the form

$$S(H, T) = \text{const.} \qquad (1432, 2)$$

In a crystal containing paramagnetic ions, at not too high temperature, there are only two significant contributions to the entropy, a contribution $S^{ac}$ of the acoustical modes and a contribution $S^{sp}$ of the electronic spins. We therefore rewrite (2) in the more explicit form

$$S^{ac}(T) + S^{sp}(H, T) = \text{const.} \qquad (1432, 3)$$

For an understanding of the efficiency of the use of a magnetic field for producing changes of temperature, the point of fundamental importance is the following. Whereas $S^{ac}(T)$ is positive and decreases as the temperature decreases, $S^{sp}(H, T) - S^{sp}(0, T)$ is negative, and, for a given value of $H$, its magnitude increases as the temperature decreases. It is therefore immediately obvious that the lower the temperature the more important become variations of the term $S^{sp}$ relative to variations of the term $S^{ac}$. We may therefore expect changes of temperature associated with adiabatic variation of the magnetic field to be more important at low temperatures than at high temperatures. We now verify this expectation and obtain quantitative relations by using the formulae of the preceding section.

We have already mentioned that at temperatures below 10° K. we may safely assume $S^{ac}$ to be of the form (1431, 5) and $S^{sp}$ to be of the form (1431, 4), and these values have to be substituted into (3). Usually $\Theta_D$ has a value such that $S^{ac}$ becomes inappreciable somewhere between 5° K. and 1° K. Formula (3) then reduces to

$$S^{sp}(H, T) = \text{const.} \qquad (1432, 4)$$

In virtue of (1431, 4) this is equivalent to

$$x = \text{const.} \quad (S \text{ const.}), \qquad (1432, 5)$$

$$T \propto H \quad (S \text{ const.}). \qquad (1432, 6)$$

Suppose that a magnetic field is applied to a suitable paramagnetic crystal, say ammonium ferric alum, and it is then cooled to 4° K. by means of liquid helium. If the crystal is then insulated and the magnetic field reduced to a quarter of its original value, the temperature will according to (6) fall to 1° K. This is clearly illustrated in Fig. 8, which is due to Simon.* The part of the diagram to the left of 1° K. will be discussed later and for the moment should be ignored. If we compare the field strengths at 4° K. and 1° K. for equal entropy, we notice that the former are almost exactly four times the latter. At higher temperatures the relation (6) between $T$ and $H$ is no longer accurate, because of the contribution of the lattice vibrations to the entropy.

* Simon, *Conference on Magnetism* (Strasbourg, May 1939).

The method just described has been used in recent years especially by* De Haas, Wiersma and Kramers at Leiden, by Giauque and MacDougall at Berkeley and by Simon and Kurti at Oxford. It has been used to reach temperatures below 0·01° K.; the low limit to the attainable temperature will be described in the succeeding sections.

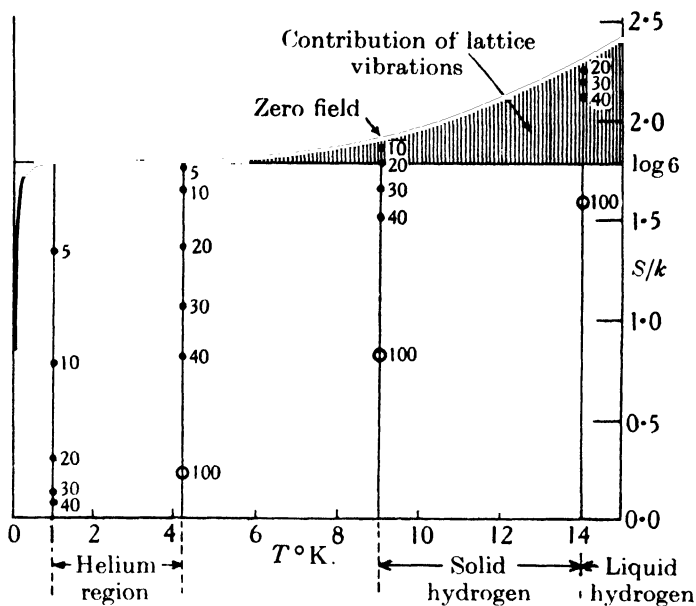



Fig. 8. Molecular entropy of $NH_4Fe(SO_4)_2\,12H_2O$ according to Simon. Numbers scattered over diagram denote magnetic field strength in Kgauss.

**§ 1433. Unattainability of absolute zero.** If formula (1432, 6) were accurate, then by adiabatic reduction of the magnetic field to zero one would reach $T = 0$, in contradiction to the principle formulated in § 538 and called the third law of thermodynamics. Formula (1431, 4), however, from which formula (1432, 6) was derived, becomes inaccurate before $T = 0$ is reached. Actually there are two distinct effects which invalidate these formulae.

Formula (1431, 4) depends on the assumption that in the absence of a magnetic field each paramagnetic ion is in a $(2S+1)$-fold degenerate state. This is not strictly true; it is true only in so far as one ignores the Stark effect of the crystalline field on the spins. We have already in § 1415 described how

* For detailed references to the numerous papers up to 1936 see for example Giauque, *Proc. 7th Int. Cong. Refrigeration* (1936); *Ind. Eng. Chem.* **28**, 743 (1936).

this field destroys the orbital degeneracy so that at low temperatures the ions are all effectively in an S state. We also mentioned that this same field, through the coupling between the orbital motions and the spins, can also act on the spins but to an incomparably weaker extent. The effect of this is that what we have hitherto regarded as a $(2S+1)$-fold degenerate S level in fact consists of several levels, but the separation between these levels is only about $10^{-1}$ deg. Consequently at temperatures where $T \gg 10^{-1}$ we are justified in ignoring these separations and treating the group of levels as a single $(2S+1)$-fold degenerate level. This is the procedure we have adopted hitherto, but it is no longer allowable when $T$ becomes comparable with $10^{-1}$. This Stark effect on the spins will be discussed in the following section.

The other effect which invalidates formula (1431, 4) at sufficiently low temperatures is the interaction between the paramagnetic ions. We have hitherto regarded these ions as completely independent of one another, so far as their orientations are concerned. Actually there is an interaction energy between every pair of magnetic ions depending on their mutual orientations. Consequently it is only an approximation to regard the assembly as composed of $N$ independent magnets, but the approximation is allowable as long as the interaction energies between pairs of ions is small compared with $kT$. The temperature at which this condition fails will be the lower, the farther apart are the paramagnetic ions. By choosing a crystal in which the paramagnetic ions are greatly diluted, one can make this temperature as low as one pleases, but obviously the practical utility of this is limited; for the increase in the volume of crystal containing a given number of ions would soon become a disadvantage outweighing any advantage of the diminution of the magnetic interaction between the ions. We shall consider this magnetic interaction between the ions in § 1435.

**§ 1434. Crystalline Stark effect on the spins.** The magnitude and nature of the crystalline Stark effect on the spins, like the corresponding effect on the orbital motions, depend on the symmetry of the field and on the multiplicity of the degenerate state. We shall confine our discussion to a field with cubic symmetry acting on an ion in an $^8$S state, that is to say having $2S+1 = 8$. The treatment therefore applies particularly to the $Gd^{+++}$ ion. The required quantal treatment has been given by Van Vleck and Penney,* and applied to this problem by Hebb and Purcell.† It is found that the cubic field splits the $^8$S state into two doubly degenerate levels and one quadruply degenerate level. The latter lies between the two former and the spacings are in the ratio 3:5. Thus the electronic partition

* Van Vleck and Penney, *Phil. Mag.* **17**, 961 (1934).
† Hebb and Purcell, *J. Chem. Phys.* **5**, 342 (1937).

function $e(T)$ in the absence of an external field is either

$$e(T) = 2\{1+2e^{-3\Theta_K/8T}+e^{-\Theta_K/T}\} \tag{1434, 1}$$

or

$$e(T) = 2\{1+2e^{-5\Theta_K/8T}+e^{-\Theta_K/T}\}, \tag{1434, 2}$$

where $k\Theta_K$ is the over-all energy separation. It has not yet been possible to predict theoretically which of (1) and (2) is correct. Comparison with experiment slightly favours (1), and this form is provisionally assumed to be the correct one. A crystalline field of lower symmetry could split the quadruply degenerate level into two doubly degenerate levels, but no further splitting by a Stark effect is possible.

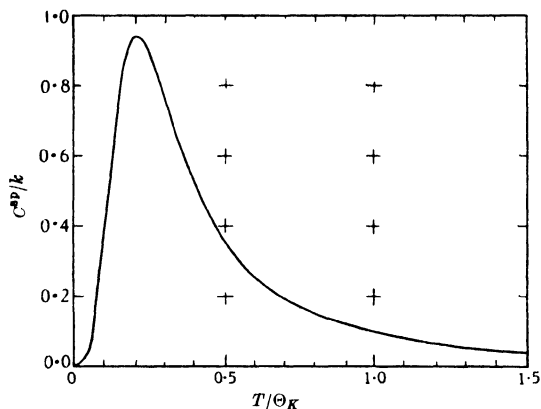



Fig. 9. Theoretical electronic contribution to the heat capacity of an ion in an $^8S$ state, when the crystalline field has cubic symmetry and magnetic interactions between the ions are neglected. The curve should apply approximately to salts of $Gd^{+++}$ in which these ions are very dilute, e.g. $Gd(O_3SC_6H_4NO_2)_3.7H_2O$.

From (2) we obtain the orientational electronic entropy per ion in the absence of an external field by use of the formula

$$\frac{S^{sp}}{k} = \frac{\partial}{\partial T}\{T\log e(T)\}, \tag{1434, 3}$$

and the electronic heat capacity per ion in the absence of an external field by use of the formula

$$\frac{C^{sp}}{k} = T\frac{\partial^2}{\partial T^2}\{T\log e(T)\}. \tag{1434, 4}$$

In Fig. 9 we show $C^{sp}/k$ calculated according to (1) and (4) as a function of $T/\Theta_K$. We see that the electronic heat capacity has a maximum near $T = 0{\cdot}2\Theta_K$, and is appreciable in the range of $T$ from $0{\cdot}05\Theta_K$ to $1{\cdot}5\Theta_K$.

Corresponding to the peak in the electronic heat capacity, there is a rapid change of entropy in the neighbourhood $T \simeq \Theta_K$. As the temperature is lowered the electronic entropy per ion falls from $k \log 8$ for $T \gg \Theta_K$ to $k \log 2$ for $T \ll \Theta_K$. The entropy calculated according to (3) is plotted against $T$ in Fig. 10 for $\Theta_K = 1{\cdot}4°$.

For comparison with experiment one should choose a compound in which the $Gd^{+++}$ ions are at a high dilution so as to justify neglect of interaction between the spins. Hebb and Purcell accordingly use the data of MacDougall and Giauque* on the salt $Gd(O_3SC_6H_4NO_2)_3.7H_2O$. These data are included in Fig. 10 where the value $\Theta_K = 1{\cdot}4°$ has been assumed to obtain the

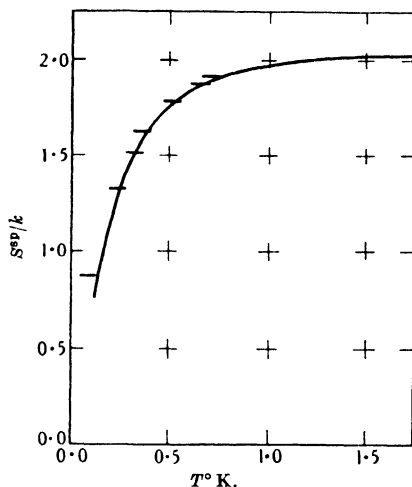



Fig. 10. Molecular entropy of $Gd(O_3SC_6H_4NO_2)_3.7H_2O$. Curve: calculated theoretically by Hebb and Purcell assuming $\Theta_K = 1{\cdot}4°$. — represent experimental data of MacDougall and Giauque within the slight uncertainty in the temperature scale.

best possible fit. With regard to the experimental data, we would mention that the entropy of each point is known accurately but there is a small uncertainty with regard to the temperature. We postpone elaboration of this point to § 1438.

Hebb and Purcell have also derived a formula for the magnetic susceptibility. For $T \simeq \Theta_K$ the formula is complicated, as we should expect; we need only recall an analogous complexity in the susceptibility of $Sm^{+++}$ at ordinary temperatures, mentioned in § 1413.

**§ 1435. Magnetic interaction of spins.** We turn now to the effect of the magnetic interaction of the spins. We can no longer construct an

* MacDougall and Giauque, *J. Am. Chem. Soc.* **58**, 1032 (1936).

electronic partition function for each paramagnetic ion, but only an electronic partition function for the whole assembly. The method of attack is due to Waller,* and has been developed in great detail by Van Vleck.† It is in fact the method subsequently applied by Kirkwood to order-disorder in alloys and already described in § 1311. Essentially the method consists in expanding the partition function in powers of $E_r/kT$, where $E_r$ denotes the energy of the assembly in the state $r$. One obtains for the partition function of the assembly

$$(2S+1)^N\left\{1-\frac{E_{Av}}{kT}+\frac{(E^2)_{Av}}{2!\,k^2T^2}+\frac{(E^3)_{Av}}{3!\,k^3T^3}+\dots\right\}, \qquad (1435,1)$$

where the subscript $Av$ denotes the unweighted average value evaluated quantally, that is to say the diagonal sum of the matrix for $E^r$ divided by the number of rows or columns; the factor $(2S+1)^N$ is merely the total number of states of an assembly of $N$ magnets, each of which can have $(2S+1)$ orientations. It can be verified that $E_{Av}$ is zero. The evaluation of $(E^2)_{Av}$ in the absence of an external field was performed by Waller. The result is

$$(E^2)_{Av}=\frac{N}{6}\,16S^2(S+1)^2\beta^4V^{-2}Q. \qquad (1435,2)$$

Here $V$ denotes the volume per magnetic ion and $Q$ is a pure number defined by

$$Q=2V^2\Sigma_j r_{ij}^{-6}, \qquad (1435,3)$$

where $r_{ij}$ denotes the distance from a given magnetic ion $i$ to any other magnetic ion $j$. We have already met the sum $Q$ in § 1429. It is convenient to define a characteristic temperature $\Theta_m$ by

$$k\Theta_m=\frac{4S(S+1)\beta^2}{V}. \qquad (1435,4)$$

Substituting (2) into (4) and (4) into (1), we obtain for the assembly's partition fraction

$$(2S+1)^N\left\{1+N\frac{Q}{12}\frac{\Theta_m^2}{T^2}+O\left(\frac{\Theta_m^3}{T^3}\right)\right\}. \qquad (1435,5)$$

We derive from (5) for the contribution of the magnetic spins to the free energy, the energy and the entropy

$$\frac{F^{\text{sp}}}{NkT}=-\log(2S+1)-\frac{Q}{12}\frac{\Theta_m^2}{T^2}+O\left(\frac{\Theta_m^3}{T^3}\right), \qquad (1435,6)$$

$$\frac{E^{\text{sp}}}{NkT}=-\frac{Q}{6}\frac{\Theta_m^2}{T^2}+O\left(\frac{\Theta_m^3}{T^3}\right), \qquad (1435,7)$$

$$\frac{S^{\text{sp}}}{Nk}=\log(2S+1)-\frac{Q}{12}\frac{\Theta_m^2}{T^2}+O\left(\frac{\Theta_m^3}{T^3}\right). \qquad (1435,8)$$

* Waller, *Zeit. Phys.* **104**, 132 (1936). † Van Vleck, *J. Chem. Phys.* **5**, 320 (1937).

The corresponding contribution to the heat capacity is

$$\frac{C^{sp}}{Nk} = \frac{Q}{6}\frac{\Theta_m^2}{T^2} + O\left(\frac{\Theta_m^3}{T^3}\right). \qquad (1435, 9)$$

Van Vleck has evaluated the higher terms as far as $(E^4)_{Av}$, but when these are significant it is doubtful whether the series converges sufficiently rapidly to be useful. The series expansion may not be used unless $T$ is appreciably greater than $\Theta_m$; it is still uncertain how great $T/\Theta_m$ is required to be.

According to (9) we see that as we decrease $T$ there will be a rise in the heat capacity as we approach $T \simeq \Theta_m$. This rise in the heat capacity is equivalent to a fall in the entropy represented by the second term of (8). It is physically obvious that this fall cannot continue indefinitely, since $S^{sp}$ cannot become negative, but must tend to zero as $T \to 0$ to preserve the third law of thermodynamics. This means that at $T = 0$ the orientations of the magnetic ions will be arranged in a unique perfectly ordered manner. It is still a matter of uncertainty exactly what this ordered state should be. In particular it is uncertain whether or not in this state the crystal has a permanent magnetic moment in the absence of an external field, that is to say whether the crystal becomes ferromagnetic. It is probable, but not certain, that the answer depends on the shape of the crystal.

In general the effects due to magnetic interactions will be superposed on the Stark effect of the crystalline field, discussed in § 1434, and the situation is then complicated. There is a simplification for ions in a doublet state, effectively a $^2$S state, such as the $Ti^{+++}$ ion. The free $Ti^{+++}$ ion has one $4f$-electron and is in a $^2$F state, but the crystalline field quenches the orbital momentum at comparatively high temperatures so that in the crystal the ion is effectively in a $^2$S state. The crystalline field is, however, without effect on the spin. Hence for compounds containing $Ti^{+++}$ ions there is only the magnetic interaction between the ions to be considered.

Hebb and Purcell* have accordingly applied formula (13) to the alum $CsTi(SO_4)_2 . 12H_2O$. As the arrangement of $Ti^{+++}$ ions is cubic face-centred, $Q = 14{\cdot}4$. In formula (4) defining $\Theta_m$ we have to use $S = \frac{1}{2}$ and $\mathbf{N}V = 290$ cm.$^3$ This gives $\Theta_m = 0{\cdot}0038$. There are experimental data for the heat capacity obtained by Kurti and Simon,† but there is still some uncertainty with regard to the temperature scale.‡ Within this uncertainty the agreement between the calculated and observed heat capacities is reasonable.

Van Vleck§ has by the same method derived a series expansion for the susceptibility, but it is not safe to use it unless $T \gg \Theta_m$. The reader who is interested should read Van Vleck's papers.

* Hebb and Purcell, *J. Chem. Phys.* **5**, 344 (1937).

† Kurti and Simon, unpublished measurements.

‡ See Van Vleck, *J. Chem. Phys.* **6**, 81 (1938). § Van Vleck, *J. Chem Phys.* **5**, 320 (1937).

**§ 1436. General behaviour below 1° K.** We can now describe briefly what we may expect to be the general behaviour of a crystal containing paramagnetic ions at temperatures below 1° K. We shall consider in particular the entropy per magnetic ion. As we have already mentioned, the contributions of the lattice vibrations are entirely negligible below about 5° K. At temperatures from about 5° K. to 1° K. the electronic entropy per ion is given by

$$S^{\mathrm{sp}}/k = \log(2S+1). \tag{1436, 1}$$

Somewhere in the region $T \simeq 10^{-1}$, as a result of the crystalline Stark effect on the spins, the electronic entropy falls to a value

$$S^{\mathrm{sp}}/k = \log 2. \tag{1436, 2}$$

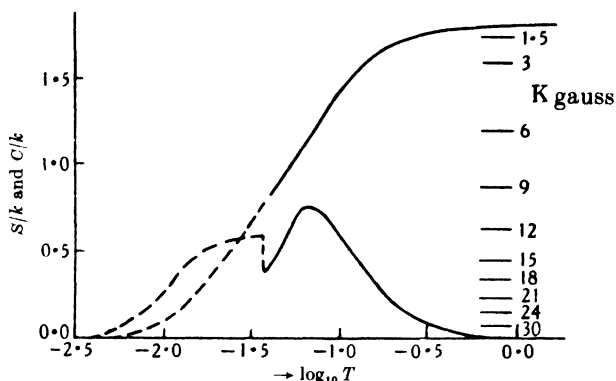



Fig. 11. Molecular entropy and heat capacity below 1° K. of $NH_4Fe(SO_4)_2.12H_2O$ according to Debye. Curves based partly on theory and partly on experiment. On the right are given the entropy values at 1° K. in magnetic fields of the strengths shown.

The magnetic interactions between the ions produce a further fall in the entropy to a value

$$S^{\mathrm{sp}}/k = 0. \tag{1436, 3}$$

The more dilute the magnetic ions, the lower the temperature where this fall occurs. Very roughly speaking we may say that it occurs in the region $T \simeq 10^{-2}$. The regions of the two drops in entropy, however, may and often will overlap. Corresponding to each step in the drop of entropy there is a peak in the heat capacity. The behaviour of ammonium ferric alum has been discussed semi-quantitatively by Debye* and is illustrated in Fig. 11, where the abscissa is $\log_{10} T$. The curve for $S/k$ is equivalent to the part of the curve at the extreme left of Fig. 8, but owing to the change of scale the details are here more apparent.

From the general shape of the curves in Fig. 11 we can draw certain important conclusions. We see that, however strong the initial field, adiabatic

* Debye, *Ann. Phys.* **32**, 85 (1938).

demagnetization will never enable one to reach $T = 0$. This is in agreement with the third law of thermodynamics. We also observe that the temperature reached by adiabatic demagnetization varies rather slowly with the initial field strength and is roughly speaking characteristic of the substance used. For example, if one can use magnetic fields up to 10 K gauss, we see that ammonium ferric alum is a suitable substance for obtaining temperatures between 0·04° K. and 0·08° K. If, however, one wishes to attain temperatures in some different region, one should use a different substance having a peak in its heat capacity in the desired region. Since the heat capacity at the final temperature of an adiabatic demagnetization will always be rather high, it should be easy to maintain the low temperature constant over a long time, as has in fact been verified experimentally.*

**§ 1437. Principles of temperature measurement.** Before describing the method used for measuring temperatures below 1° K., we shall digress to discuss the general principles underlying any measurement of absolute temperature. In particular we wish to emphasize the distinction between three methods which we may call the *purely thermodynamic method*, *the semi-thermodynamic method* and the *indirect method* respectively.

Let us consider an assembly whose thermodynamic state is completely specified by an empirical temperature $t$ and a geometrical parameter $x$. The problem is to determine the absolute temperature $T$ as a function of the empirical temperature $t$. Usually the complete description of the thermodynamic state of the assembly will require the specification of more than one geometrical parameter $x$, but we may often assume that all except one of these parameters is either held constant or is irrelevant. For the sake of brevity, we here assume that this is the case. Moreover, to avoid making the argument too abstract we shall provisionally choose for the parameter $x$ the volume $V$, but we would emphasize that, if we replace $V$ by a suitable magnetic or other quantity, then *mutatis mutandis* the argument will remain valid.

From the thermodynamic formula

$$\frac{\partial(F/T)}{\partial(1/T)} = E, \tag{1437, 1}$$

which embodies the second law of thermodynamics, we obtain by differentiating with respect to $V$

$$\frac{\partial(P/T)}{\partial(1/T)} = -\left(\frac{\partial E}{\partial V}\right)_T = -\left(\frac{\partial E}{\partial V}\right)_t. \tag{1437, 2}$$

Let us suppose that it has been found experimentally that, at a selected

* See Simon, Conference on Magnetism (Strasbourg, May 1939).

empirical temperature $t$, the pressure can be accurately expressed by a formula such as

$$P = \frac{A}{V} + \frac{B}{V^2} + \frac{C}{V^3}, \qquad (1437,3)$$

where $A$, $B$, $C$ are constants at the given temperature $t$, but depend on $t$. The number and form of the terms in (3) is irrelevant. We have chosen for illustration a form which is in fact an accurate representation of the experimental data for any gas, but the argument would be unaffected if we included, for example, a term independent of $V$, or positive powers of $V$ or a term in $\log V$. Let us further suppose that by accurate repetition of Joule's experiment a similar experimental formula has been obtained for $(\partial E/\partial V)_t$. We write this formula as

$$-\left(\frac{\partial E}{\partial V}\right)_t = \frac{A'}{V} + \frac{B'}{V^2} + \frac{C'}{V^3}, \qquad (1437,4)$$

where $A'$, $B'$, $C'$ are independent of $V$ but depend on $t$.

By substitution of (3) and (4) into (2) and equating coefficients, we deduce

$$\frac{d\{A(t)/T\}}{d(1/T)} = A'(t), \quad \frac{d\{B(t)/T\}}{d(1/T)} = B'(t), \quad \frac{d\{C(t)/T\}}{d(1/T)} = C'(t). \qquad (1437,5)$$

Corresponding to each term in the series expansions we have a differential equation relating $t$ to $T$, and in principle each of these equations determines the functional relation between $T$ and $t$. These equations are, however, usually neither sufficiently simple nor sufficiently accurate (numerically) to be useful for the purpose of fixing the relation between $T$ and $t$. To obtain accuracy it will obviously be desirable to use the coefficients of the dominant term in the series. We shall now discuss a particularly favourable example.

Let us suppose that, as a result of experiment, it is found that one of the coefficients in (4) (preferably that of the dominant term) is zero, while that of the corresponding term in (3) is non-zero. For definiteness let us suppose that it has been found experimentally that

$$A'(t) = 0, \quad A(t) \neq 0. \qquad (1437,6)$$

We can now immediately integrate the first equation (5) and obtain

$$A(t) \propto T. \qquad (1437,7)$$

In other words

$$\operatorname*{Lt}_{V\to\infty} PV = A(t) \propto T. \qquad (1437,8)$$

This completes our description of the *purely thermodynamic method*. We can confidently say that if Joule's experiment were performed on any permanent gas with sufficient accuracy, it would be found that

$$A'(t) = 0, \qquad (1437,9)$$

and so the relations (8) would be established on a basis of pure experiment

combined with classical thermodynamics. So far as we know *such experiments have never been performed* with an accuracy even remotely approaching that required to substantiate the validity of (9). We can even make the more sweeping statement that the absolute temperature scale has probably never been determined by the purely thermodynamic method.

We turn now to describe the semi-thermodynamic method. This method consists essentially in the substitution of knowledge based on molecular theory for direct experimental measurements. In the present state of our knowledge we can confidently assert that any permanent gas consists of molecules between which the interactions are of a short range nature. As soon as we accept the correctness of this assertion we can deduce by elementary reasoning that

$$\mathop{\mathrm{Lt}}_{V-} V\left(\frac{\partial E}{\partial V}\right)_t = 0. \qquad (1437, 10)$$

This is equivalent to (9), and then by thermodynamics we can derive (8). This completes the description of the *semi-thermodynamic method*. It is in fact the method on which all gas thermometry has been based.

Finally we wish to describe an indirect method, which has never been used in gas thermometry, but is nevertheless instructive, because it is the precise analogue of the method now in use for measuring temperatures below 1° K. Let us consider two reversible adiabatic changes, which we denote schematically by

$$(t_i, V_i) \to (t_f, V_f), \quad (t_i + \delta t_i, V_i + \delta V_i) \to (t_f + \delta t_f, V_f), \qquad (1437, 11)$$

where the subscripts $i$, $f$ refer to the initial and final states respectively. It should be noticed that the two processes have been chosen so that the two final states have the same volume $V_f$, but have empirical temperatures differing by $\delta t_f$. We suppose that the absolute temperatures of the initial states have been determined, say by the thermodynamic method, but that those of the final states are unknown. We suppose further that both the initial states correspond to those of an almost perfect gas, so that by applying the laws of perfect gases and the required small corrections for imperfections, one can calculate the entropy difference between the two initial states. Since by supposition both the processes are reversible and adiabatic, the associated entropy change is zero for both. The difference $\delta S_f$ in entropy of the two final states is thus equal to that of the two initial states, and is known. If one makes the single experiment of measuring the energy difference $\delta E_f$ between the two final states, then from the thermodynamic relation

$$T = (\partial E/\partial S)_V \qquad (1437, 12)$$

we can obtain $T_f$ by merely dividing $\delta E_f$ by $\delta S$. This completes the descrip-

tion of the *indirect method*, by which we can deduce the temperature $T_f$, in a range where one cannot use a gas thermometer, from the known properties of the assembly at a temperature $T_i$ in a different temperature range, where $T_i$ can be determined by a gas thermometer.

**§ 1438. Measurement of temperatures below 1° K.** We shall now discuss briefly possible methods of measuring temperatures below 1° K., where gas thermometry is no longer possible.

A purely thermodynamic method is in principle possible by using as the geometrical variable $x$ a suitable magnetic quantity. We shall not here write down the analogue of (1437, 2). There are several alternative formulae, thermodynamically equivalent to one another, but applicable under different conditions. The method would require the determination of a free energy change and of an energy change to which formula (1437, 1) could then be applied. The determination of a free energy change requires the measurement of an (isothermal) susceptibility and offers no great difficulty. The determination of the corresponding energy change, on the other hand, offers great experimental difficulty. In practice magnetic fields are maintained by electromagnets fed by batteries or dynamos, and it would be necessary to take acount of the extra energy supplied by the battery or dynamo when the magnetic specimen is being moved into the field; this is not easy. The method has not yet been used, and it is doubtful if it ever will be.

We now turn to a useful semi-thermodynamic method for measuring the temperature of certain paramagnetic substances. If on the strength of theory one is confident that the carriers of magnetism are in ground states from which the lowest excited states are separated by differences great compared with $kT$, and that the interaction between these elementary magnets is negligible, then by statistical mechanics we deduce Curie's law:

$$\kappa \propto 1/T. \qquad (1438, 1)$$

Under these conditions one can determine the temperature by measuring the susceptibility and using (1). This method, however, is of limited applicability. In particular it is not applicable at the final temperature reached by an adiabatic demagnetization, because as we saw in § 1432, such a temperature is always in the region where there is an anomalous heat capacity, and Curie's law is not then valid. However, formula (1) may still be used to define an empirical temperature, which is likely to be not very different from the Kelvin temperature.* The values so calculated are sometimes called *temperatures on the Curie scale.*†

* See Kurti and Simon. *Phil. Mag.* **24**, 849 (1938).

† Not to be confused with the Curie temperature described in §§ 1445–1448.

The method in actual use for determining absolute temperatures below 1° K. is an indirect one, precisely analogous to that described in § 1437. Consider two adiabatic demagnetizations represented by

$$(t_i, H_i) \to (t_f, 0), \quad (t_i, H_i + \delta H_i) \to (t_f + \delta t_f, 0). \qquad (1438, 2)$$

If the initial conditions are such that the absolute temperature $T_i$ has been determined, say by a gas thermometer, and the experimental substance obeys Curie's law, then the entropy difference $\delta S_i$ between the two initial states can be calculated. Since both processes are reversible and adiabatic, the associated entropy change is zero, and the entropy difference $\delta S_f$ between the two final states is equal to $\delta S_i$. To determine the absolute temperature $T_f$ corresponding to $t_f$, all that is required is a single experimental determination of the energy difference $\delta E_f$ between the two final states. Use of the thermodynamic relation

$$(\partial E/\partial S)_{H=0} = T \qquad (1438, 3)$$

then gives directly the value of $T_f$. The only experimental difficulty is to find a suitable source of energy utilizable at such low temperatures. This difficulty has been overcome by Kurti and Simon* by using bombardment by gamma rays, and by Giauque and MacDougall,† by using an induced electric current in a gold wire.

Only a few results of measurements of this kind have yet been published. Giauque and MacDougall, using the salt $Gd(PMo_{12}O_{40}).30H_2O$, could not detect with certainty any difference between the absolute scale and the Curie scale of temperature down to about 0·3°. Kurti and Simon using ammonium ferric alum found significant differences in the neighbourhood of 0·03°.

**§ 1439. Magnetic susceptibilities of metals. Susceptibility due to electron spin.** We have still to discuss the magnetic susceptibilities of metals. We postpone all reference to ferromagnetism to § 1445 and confine ourselves for the present to paramagnetic metals. In these the carriers of the magnetic properties are the electrons in incomplete bands, and we have to use Fermi-Dirac statistics as in Chapter XI. There are two contributions to the susceptibility, the one positive from the orientations of the electron spins, the other negative from the translational motion of the electrons. We shall discuss these two effects in turn, using Sommerfeld's simple model of a gas of free electrons already described in detail in Chapter XI.

* Kurti and Simon, *Phil. Mag.* **26**, 840 (1938), where full references are given to work by other experimenters.

† Giauque and MacDougall, *J. Am. Chem. Soc.* **60**, 376 (1938).

The theory of the paramagnetic susceptibility due to the spin of a gas of free electrons is due to Pauli,* and was the earliest application of Fermi-Dirac statistics. It is convenient to use the grand partition function $\Xi$ for an assembly of free electrons in a volume $V$. We use as zero of energy the state of rest of all electrons inside the metal. If we denote by $\Xi_0$ the value of $\Xi$ in the absence of an external field, it can be verified that

$$\Xi_0 = 2\frac{(2\pi m_e kT)^{\frac{3}{2}} V}{h^3}\frac{2}{\pi^{\frac{1}{2}}}\int_0^\infty x^{\frac{1}{2}}\log(1+\lambda e^{-x})\,dx. \qquad (1439, 1)$$

The value of $\lambda$ is determined by

$$N = \lambda(\partial \Xi_0/\partial\lambda)_{T,V}, \qquad (1439, 2)$$

if $N$ is the number of free electrons. Using (2) in (1), we find

$$N = 2\frac{(2\pi m_e kT)^{\frac{3}{2}} V}{h^3}\frac{2}{\pi^{\frac{1}{2}}}\int_0^\infty \frac{x^{\frac{1}{2}}\,dx}{1+e^x/\lambda}, \qquad (1439, 3)$$

which is the same as formula (1102, 8); this verifies the correctness of (1).

In a magnetic field $H$ each electron has an extra energy $\mp\beta H$ according to its orientation down or against the field. The grand partition function then becomes

$$\Xi = \frac{(2\pi m_e kT)^{\frac{3}{2}} V}{h^3}\frac{2}{\pi^{\frac{1}{2}}}\left\{\int_0^\infty x^{\frac{1}{2}}\log(1+\lambda e^{-(x-\beta H/kT)}) + \int_0^\infty x^{\frac{1}{2}}\log(1+\lambda e^{-(x+\beta H/kT)})\right\}, \qquad (1439, 4)$$

and the average moment $\bar{\mu}$ per electron parallel to the field is given by

$$N\bar{\mu} = kT(\partial\Xi/\partial H)_{T,\lambda}. \qquad (1439, 5)$$

We can expand (4) in powers of $\beta H/kT$ and find

$$\Xi = \Xi_0 + \frac{1}{2}\left(\frac{\beta H}{kT}\right)^2\frac{\partial^2\Xi_0}{(\partial\log\lambda)^2} + O\left(\frac{\beta H}{kT}\right)^4. \qquad (1439, 6)$$

Assuming as usual that we may neglect saturation effects, the values of $N$ and $N\bar{\mu}$ from (2) and (5) are given with sufficient accuracy by

$$N = \frac{\partial\Xi_0}{\partial\log\lambda}, \qquad (1439, 7)$$

$$N\frac{\bar{\mu}}{\beta} = \frac{\beta H}{kT}\frac{\partial^2\Xi_0}{(\partial\log\lambda)^2}. \qquad (1439, 8)$$

By the method of § 1104, we can deduce for $\Xi_0$

$$\Xi_0 = 2\frac{(2\pi m_e kT)^{\frac{3}{2}} V}{h^3}\frac{8}{15\pi^{\frac{1}{2}}}(\log\lambda)^{\frac{5}{2}}\left\{1+\frac{5\pi^2}{8}(\log\lambda)^{-2}\right\}, \quad (1439, 9)$$

* Pauli, *Zeit. Phys.* **41**, 81 (1927).

neglecting higher powers of $(\log\lambda)^{-2}$. From (7) and (9) we derive

$$N = 2\frac{(2\pi m_e kT)^{\frac{3}{2}}V}{h^3}\frac{4}{3\pi^{\frac{1}{2}}}(\log\lambda)^{\frac{3}{2}}\left\{1+\frac{\pi^2}{8}(\log\lambda)^{-2}\right\}. \quad (1439, 10)$$

Similarly from (8) and (9) we derive

$$N\frac{\bar{\mu}}{\beta} = \frac{\beta H}{kT}2\frac{(2\pi m_e kT)^{\frac{3}{2}}V}{h^3}\frac{2}{\pi^{\frac{1}{2}}}(\log\lambda)^{\frac{1}{2}}\left\{1-\frac{\pi^2}{24}(\log\lambda)^{-2}\right\}. \quad (1439, 11)$$

Dividing (11) by (10) we find

$$\frac{\bar{\mu}}{\beta} = \frac{\beta H}{kT}\tfrac{3}{2}(\log\lambda)^{-1}\left\{1-\frac{\pi^2}{6}(\log\lambda)^{-2}\right\}. \quad (1439, 12)$$

If we introduce the energy $\epsilon^*$ defined by

$$\epsilon^* = \frac{h^2}{8m_e}\left(\frac{3N}{\pi V}\right)^{\frac{2}{3}}, \quad (1439, 13)$$

so that in the absence of any external field there are just $N$ states of energy not exceeding $\epsilon^*$, we can rewrite (10) as

$$1 = \left(\frac{kT}{\epsilon^*}\right)^{\frac{3}{2}}(\log\lambda)^{\frac{3}{2}}\left\{1+\frac{\pi^2}{8}(\log\lambda)^{-2}\right\}, \quad (1439, 14)$$

or correct to the same order

$$\log\lambda = \frac{\epsilon^*}{kT}\left\{1-\frac{\pi^2}{12}\left(\frac{kT}{\epsilon^*}\right)^2\right\}, \quad (1439, 15)$$

which is the same as equation (1104, 9). Substituting from (15) into (12) we obtain finally

$$\frac{\bar{\mu}}{\beta} = \frac{3}{2}\frac{\beta H}{\epsilon^*}\left\{1-\frac{\pi^2}{12}\left(\frac{kT}{\epsilon^*}\right)^2\right\}. \quad (1439, 16)$$

We have already verified in Chapter XI that $\epsilon^*/k \simeq 10^4$ deg. We may therefore neglect $(kT/\epsilon^*)^2$ compared with unity, and (16) simplifies to

$$\frac{\bar{\mu}}{\beta} = \frac{3}{2}\frac{\beta H}{\epsilon^*} \quad \text{(spin only)}. \quad (1439, 17)$$

**§ 1440. Paramagnetic metals continued. Susceptibility due to translational motion of electrons.** In classical theory the energy of an electron is not affected by a magnetic field (apart from its energy of orientation, if it is thought to have a permanent moment due to spin), and therefore Maxwell's and Boltzmann's distribution laws continue to apply to its translatory motion unaltered. If therefore one considers the current carried by the electrons in any direction past any fixed point, this current is always exactly zero whether or not a magnetic field is acting. A gas of classical free electrons can therefore have no susceptibility, apart from that due to spin, since no current is generated by the magnetic field. It is, however, easy to

cast doubt on this argument by considering the paths of the actual electrons, which (in the plane normal to $H$) are all circles in the same sense about the field, each one making a diamagnetic contribution. The contradiction is removed when it is remembered that the electron gas must have a boundary, and that near the boundary the average movement of the electrons must by repeated reflexion be a creep round the boundary in the opposite sense (see Fig. 12). These few large orbits exactly balance the effect of the many smaller orbits in which electrons circulate in the ordinary direction.*

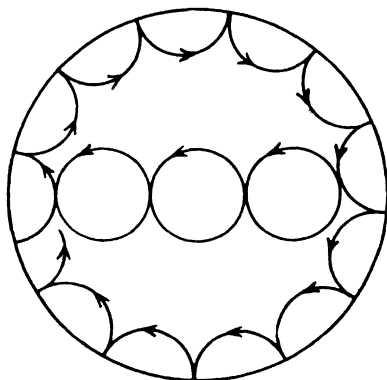



Fig. 12. Illustrating the absence of orbital magnetism for classical free electrons.

In the quantum theory, however, this balance is no longer exact, and diamagnetism results. The reason for this is that in the quantum theory the eigen functions are modified by the boundary, for example they must tend to zero at a rigid wall, and further that even apart from this boundary effect the possible momenta normal to the field which can vary continuously in the absence of a magnetic field are quantized in the presence of the field, facts which destroy the perfect classical balance. This was first pointed out by Landau.†

It can be shown that the translational energy levels of electrons in a box of volume $V$ in a uniform field $H$ along the $z$-direction are of the form

$$\epsilon = \tfrac{1}{2}p_z^2/m_e + (2n+1)\beta H \quad (n = 0, 1, 2, \ldots) \qquad (1440, 1)$$

and that the number of translational states of given $n$ in the momentum range $p_z$, $p_z + dp_z$ is

$$V\frac{|e|\,H}{ch^2}\,dp_z = V\frac{4\pi m_e \beta H}{h^3}\,dp_z. \qquad (1440, 2)$$

* Bohr, Dissertation, *Studier over Metallernes Elektrontheori*, 105 (Copenhagen, 1911).

† Landau, *Zeit. Phys.* **64**, 629 (1930); cf. Darwin, *Proc. Camb. Phil. Soc.* **27**, 86 (1931); Sommerfeld and Bethe, *Handb. d. Physik*, **24** (2), 473 (1933).

This value must be multiplied by 2 to take account of the two directions of spin. The grand partition function is therefore

$$\Xi = 2V\frac{4\pi m_e \beta H}{h^2}\sum_{n=0}^{\infty}\int_{-\infty}^{+\infty}\log\left[1+\lambda e^{-\{\frac{1}{2}p_z^2/m_e+(2n+1)\beta H\}/kT}\right]dp_z. \quad (1440, 3)$$

The summation and integration in (3) can be performed with sufficient accuracy to give formulae for $N$ and for $N\bar{\mu}$ in terms of $\log\lambda$. We shall not give details.† Eventually one obtains

$$\frac{\bar{\mu}}{\beta} = -\frac{1}{2}\frac{\beta H}{\epsilon^*}\left\{1-\frac{\pi^2}{12}\left(\frac{kT}{\epsilon^*}\right)^2\right\}, \quad (1440, 4)$$

neglecting higher powers of $kT/\epsilon^*$ and of $\beta H/\epsilon^*$. If as usual we assume that $\epsilon^*/k \simeq 10^4$ deg., we may simplify (4) to

$$\frac{\bar{\mu}}{\beta} = -\frac{1}{2}\frac{\beta H}{\epsilon^*} \quad \text{(orbits only)}. \quad (1440, 5)$$

We observe that the translational degrees of freedom of the electrons give a negative (diamagnetic) contribution to the susceptibility.

**§ 1441. Magnetic susceptibility of alkali metals.** As already explained in Chapter XI, Sommerfeld's model, which we have used here, may be expected to apply better to the alkali metals than to other metals. It is therefore of interest to compare the susceptibilities calculated for the model with the experimental values.

The resultant susceptibility, when the spin and translational effects are superposed, is not obviously the sum of the two contributions calculated independently. The required formulae have been derived by Stoner,‡ who finds that to the first power in $H$ and to the second power in $T$ the contributions are in fact additive. Thus for the resultant average moment per electron parallel to the field he finds

$$\frac{\bar{\mu}}{\beta} = \frac{\beta H}{\epsilon^*}\left\{1-\frac{\pi^2}{12}\left(\frac{kT}{\epsilon^*}\right)^2\right\}. \quad (1441, 1)$$

If we assume one free electron per atom, we obtain for the atomic susceptibility

$$\kappa = \frac{\beta^2}{\epsilon^*}\left\{1-\frac{\pi^2}{12}\left(\frac{kT}{\epsilon^*}\right)^2\right\}. \quad (1441, 2)$$

For comparison with the calculated values the experimental values for the alkali metals have to be corrected for the diamagnetic contributions of the metallic ions, taken from experimental data on compounds containing ions of these metals. This correction is by no means negligible, and is par-

† See, for example, Stoner, *Proc. Roy. Soc.* A, **152**, 672 (1935).

‡ Stoner, *Proc. Roy. Soc.* A, **152**, 672 (1935).

ticularly important for the larger ions of Rb and Cs. For a review of the experimental data we refer the reader to Stoner.† There are large discrepancies between the measured values of different experimenters. There is agreement between calculated and observed values within a factor of about 2, which is all that can be expected until more decisive experimental results are available.

**§ 1442. Extension of theory.** In Chapter XI we explained that many of the formulae derived for a gas of free electrons are applicable to the electrons in an incomplete band, provided $\epsilon^*$ is suitably defined. This is also the case for the formulae derived for the susceptibility due to free electrons. In the derivation of these formulae the essential assumption is that in the absence of a field the energy levels are distributed with a density proportional to the square root of the energy, that is to say

$$g(\epsilon)\,d\epsilon = A\epsilon^{\frac{1}{2}}\,d\epsilon. \qquad (1442, 1)$$

The proportionality factor $A$ is irrelevant to the derivations, provided that $\epsilon^*$ is defined by

$$N = \int_0^{\epsilon^*} g(\epsilon)\,d\epsilon = \tfrac{2}{3}A\epsilon^{*\frac{3}{2}}, \qquad (1442, 2)$$

the zero energy being taken at the bottom of the band. Since the form of $g(\epsilon)$ given by (1) is generally valid near the bottom of an electron band, the formulae should be applicable to any band which is nearly empty.

The use of the formulae can be still further extended to apply to a band that is almost full. Provided the energy levels near the top of the band are distributed according to (1), where $\epsilon$ now denotes the energy *measured downwards* from the top of the band, the formulae for $\bar{\mu}/\beta$ can be shown to be still valid, if $N$ now denotes the number of unoccupied states (holes) in the band.

We shall see that these extensions of formulae derived for free electrons are of interest in connexion with ferromagnetism.

**§ 1443. External magnetic field and demagnetizing coefficients.** We recall the distinction made in § 1424 for electric fields inside matter between the pipe field $E_p$, the crack field $E_c$ and the sphere field $E_s$. In principle one should make precisely the same distinction for magnetic fields inside matter between the pipe field $H_p$, the crack field $H_c$ and the sphere field $H_s$. The intensity of magnetization is defined as the magnetic moment per unit volume. If the value of this quantity in electromagnetic units is

† Stoner, p. 509; Van Vleck, p. 359.

denoted by $I$, we have the relations

$$H_p = H_c - 4\pi I, \qquad (1443, 1)$$

$$H_s = H_c - \tfrac{8}{3}\pi I, \qquad (1443, 2)$$

analogous to the relations between $E_p$, $E_c$ and $E_s$.

Hitherto we have justifiably completely ignored any distinction between $H_p$, $H_c$ and $H_s$, because for paramagnetic substances, and still more for diamagnetic substances, we always have $|I| \ll H$. We refer to the distinction now, because we intend shortly to discuss ferromagnetic substances, for which the ratio $I/H$ is certainly not small. Actually, when the distinction is significant the most important field strength from an experimental point of view is not one of the quantities $H_c$, $H_p$, $H_s$, but a fourth quantity $H_e$, called the external field. As its name suggests, $H_e$ denotes the contribution at the place occupied by the assembly under consideration, usually called the magnetic specimen, of all magnets and coils other than the specimen itself.

If $H_e$ is uniform throughout the specimen, then $H_c$, $H_p$ and $H_s$ will also be uniform if, and only if, the specimen is an ellipsoid. There are then linear relations between $H_e$, $H_c$, $H_p$, $H_s$, depending on the axial ratios and orientation of the ellipsoid. We shall not quote these formulae* except those for a sphere. For a sphere the derivation of the relations is extremely simple, and one finds

$$H_e = H_s. \qquad (1443, 3)$$

From (1), (2) and (3) we can derive

$$H_c = H_e + \tfrac{8}{3}\pi I, \qquad (1443, 4)$$

$$H_p = H_e - \tfrac{4}{3}\pi I. \qquad (1443, 5)$$

It is customary to call the coefficient $\frac{4}{3}\pi$ in formula (5) (or in the corresponding formulae for ellipsoids) the *demagnetizing coefficient*, a name with little rhyme or reason. One might just as reasonably call the coefficient $\frac{8}{3}\pi$ in (4) (or in the corresponding formulae for ellipsoids) a magnetizing coefficient. It would save much confusion if the names† crack field, pipe field, sphere field and external field were used more, and the term demagnetizing coefficient forgotten.

In passing we may mention that of the quantities occurring in Maxwell's equations $B$ is identical with $H_c$, while $H$ is proportional to $H_p$; the proportionality constant depends on the units and is one, if, and only if, electromagnetic units are used.‡

* See Stoner, p. 39 or a text-book on electromagnetism.

† This is with slight modification a terminology introduced by Darwin, *Proc. Roy. Soc.* A, **146**, 17 (1934).

‡ See Sommerfeld, *Zeit. Techn. Physik.* **16**, 420 (1935).

In experimental measurements on ferromagnetic substances the quantities measured are $H_e$ and $I$. We shall therefore sometimes, for brevity, write simply $H$ to denote $H_e$.

§ 1444. **Note on thermodynamic formulae.** It would take too much space to discuss all the important thermodynamic formulae for magnetic substances in magnetic fields. These formulae are more numerous than one might suppose, owing to the possibility of transformations from one form to another dependent on Maxwell's equations. There is also some ambiguity concerning the thermodynamic functions, connected with the question whether in the work of moving a magnetic specimen one includes the work supplied by batteries which feed the coils producing the field. Probably the most used, and possibly the most useful* thermodynamic function, is the function $F$ defined by

$$dF = -S\,dT - M\,dH_e, \qquad (1444, 1)$$

where $M$ ($= IV$) is the total magnetic moment of the specimen. We shall not consider the controversial, but rather unimportant, question whether this $F$ should be called the free energy; and if so, the free energy of the specimen or the free energy of the specimen plus the field. We shall rather devote a few remarks to the applicability of the formula and to the physical meaning of the work term $-M\,dH_e$.

It is to be noted that the field occurring in (1) is $H_e$, not $H_c$ nor $H_p$ nor $H_s$. Formula (1) is valid for a magnetic specimen of any size, shape and magnetic properties (except that hysteresis is excluded), provided that $H_e$ is uniform throughout the space occupied by the specimen. Incidentally we may apply formula (1) to a single atom (or ion), in which case $H_e$ includes the field due to all atoms other than the atom being considered. The formula will be used in precisely this way in discussing the theory of ferromagnetism.

In the idealized case when the field $H_e$ is produced by rigid unpolarizable permanent magnets, there can be no ambiguity concerning the physical meaning of the work term $-M\,dH_e$. In the more real case when the field is produced by electromagnets fed by batteries or dynamos, the term $-M\,dH_e$ denotes the part of the work required to move the specimen from a field of strength $H_e$ to a field of strength $H_e + dH_e$, not counting the work, if any, done by the batteries or motors to keep $H_e$ constant at each place when the specimen is moved from one place to another; in other words not counting the work required to annul the currents induced in the electromagnets by moving the specimen.

We conclude the discussion of (1) with a warning against the indiscriminate use of (1) when $H_e$ is not uniform throughout the specimen. As a

* See, for example, Stoner, *Phil. Mag.* **23**, 833 (1937).

matter of fact (1) gives the right answer in such a case, provided that $M$ is proportional to $H_e$ at constant $T$ (absence of magnetic saturation); it will not give the right answer for a ferromagnetic specimen, even in the absence of hysteresis.

From (1) we can derive various other thermodynamic formulae by elementary methods. We need only mention as an example

$$\left(\frac{\partial S}{\partial H_e}\right)_T = \left(\frac{\partial M}{\partial T}\right)_{H_e}. \tag{1444, 2}$$

Whereas $F$ in (1) is a thermodynamic potential for the variables $T$, $H_e$, the corresponding thermodynamic potential for the variables $T$, $M$ is $(F+MH_e)$. We can transform (1) to

$$d(F+MH_e) = -SdT + H_e dM, \tag{1444, 3}$$

from which we can by elementary methods derive other relations; for example

$$\left(\frac{\partial S}{\partial M}\right)_T = -\left(\frac{\partial H_e}{\partial T}\right)_M. \tag{1444, 4}$$

§ 1445. **Idealized ferromagnetism**. The essential property of a ferromagnetic is that at low temperatures there is no proportionality between magnetization and field, but a very large intensity of magnetization $I$ can be produced by a small field $H_e$. Moreover, this magnetization can persist after $H_e$ is removed, provided the temperature is sufficiently low. At constant temperature $H_e$ and $I$ are not single valued functions of each other, but the $I$-$H_e$ diagram has the well-known form called a *hysteresis loop*, indicating irreversible production of entropy.

The shape and size of the hysteresis loop is, however, not a primary property of a ferromagnetic; the hysteresis loop is highly sensitive to the precise condition of the metal; that is to say to its impurity content, its heat treatment, the amount by which its small crystals have been broken up or distorted by cold working, and so on. The fundamental property is rather that of acquiring rapidly in small fields $H_e$ a large magnetization which is then unaffected by further increase of the field and is within wide limits not sensitive to the condition of the metal. If one examines a crystal of iron or nickel, the better the crystal and the purer the metal the smaller the area of the hysteresis loop. One therefore concludes that the ideal $I$-$H_e$ curve, which the theory of ferromagnetics must begin by explaining, is a discontinuous but reversible curve of the type shown in Fig. 13. The discontinuity $+I_0 \to -I_0$ at $H_e = 0$ must be a function of $T$ which vanishes when $T$ is greater than a certain temperature $T_c$ called the Curie temperature. As $H_e$ increases at constant temperature below the Curie tempera-

ture, $I$ increases, but slowly, so that very strong fields are required to increase $I$ significantly beyond $I_0$ except near the Curie point, since $I$ is already near its saturation value $I_\infty$.

A satisfactory formal theory of ferromagnetism was first given by Weiss, using Langevin's theory for paramagnetics described in § 1411. In Langevin's theory the energy of an atom with a permanent magnetic moment $\mu_0$ at an angle $\theta$ with a magnetic field is $-\mu_0 H \cos\theta$; as we have already mentioned it is unnecessary for a paramagnetic to distinguish between $H_e$, $H_c$, $H_p$, $H_s$.

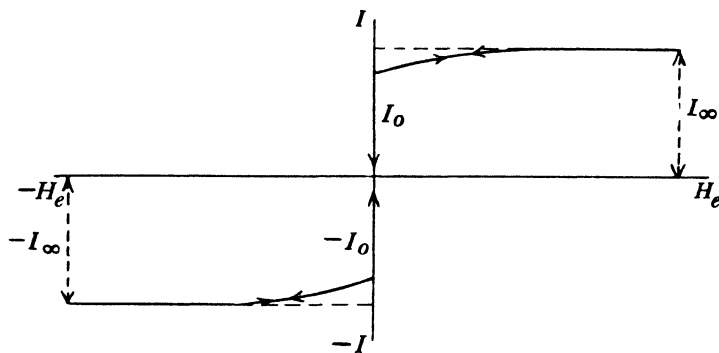



Fig. 13. The ideal $I$-$H_e$ curve for a ferromagnetic.

For a substance with a much larger susceptibility one would expect that $-\mu_0 H_s \cos\theta$ would be a better approximation than for example $-\mu_0 H_e \cos\theta$. This assumption, however, does not lead to anything like ferromagnetism at ordinary temperatures. If, following Weiss, we suppose that we have somehow overlooked in the energy some important term proportional to the magnetization, we may then write for the energy

$$-\mu_0\left(H_e + \frac{k\Theta^*}{\mu_0 I_\infty} I\right)\cos\theta. \qquad (1445, 1)$$

The reason for denoting the constant coefficient of $I$ by $k\Theta^*/\mu_0 I_\infty$ rather than by a single letter will appear later. Formula (1) embodies the essence of Weiss' theory, and the term in $I$ is often called a Weiss field. In § 1447 we shall see why such a term in fact occurs.

**§ 1446. Development and modification of Weiss' theory.** Weiss' theory in its original form was an essentially classical theory, except in so far as it assumed the existence of elementary permanent magnets of moment $\mu_0$. On the assumption that these magnets can take up all possible orientations, a straightforward application of classical statistical mechanics,

exactly parallel to the derivation of Langevin's formula (1411, 2), leads to the formula

$$\bar{\mu} = \mu_0 L\left\{\frac{\mu_0 H_e}{kT} + \frac{\Theta^*}{T}\frac{I}{I_\infty}\right\}, \tag{1446, 1}$$

where $L(x)$ denotes Langevin's function defined by

$$L(x) = \coth x - 1/x. \tag{1446, 2}$$

By using the relations $I = N\bar{\mu}/V, \quad I_\infty = N\mu_0/V,$ (1446, 3)

we can rewrite (1) in the form

$$\frac{I}{I_\infty} = L\left\{\frac{\mu_0 H_e}{kT} + \frac{\Theta^*}{T}\frac{I}{I_\infty}\right\}. \tag{1446, 4}$$

To take account of the quantal restrictions on the allowed orientations of the elementary magnets, we must replace Langevin's function in (4) by Brillouin's function

$$\frac{2S+1}{2S}\coth\frac{2S+1}{2S}x - \frac{1}{2S}\coth\frac{x}{2S}, \tag{1446, 5}$$

where $2S+1$ is the number of distinct quantal orientations. The precise behaviour of the assembly will thus depend on the value of $2S+1$, the classical theory corresponding to $S \to \infty$, but the general behaviour is not very sensitive to the value of $S$. For simplicity we shall confine our discussion to the case $S = \frac{1}{2}$, which corresponds to reality if the elementary magnets are individual electrons. The expression (5) then reduces to $\tanh x$, and formula (4) becomes

$$\frac{I}{I_\infty} = \tanh\left\{\frac{\mu_0 H_e}{kT} + \frac{\Theta^*}{T}\frac{I}{I_\infty}\right\}. \tag{1446, 6}$$

This quantal transcription of Weiss' formula is due to Heisenberg.† Investigation of formula (6) leads to the following results.

We first consider the behaviour of the assembly in the absence of an external field. Formula (6) now reduces to

$$\frac{I}{I_\infty} = \tanh\left\{\frac{\Theta^*}{T}\frac{I}{I_\infty}\right\}. \tag{1446, 7}$$

We have already met an equation of precisely this form in § 1315, where we described Bragg and Williams' approximate treatment of order-disorder in alloys. We recall that when $T > \Theta^*$ the only solution of (7) is $I = 0$, but when $T < \Theta^*$ there are two solutions of (7), one of which is still zero. It can be shown that, when there are two solutions of (7) the minimum of the free energy is that given by the non-zero value of $I$, which is therefore the stable state. Consequently, in the absence of an external field, there should be permanent magnetization below but not above the temperature $\Theta^*$. This

† Heisenberg, *Zeit. Phys.* **49**, 619 (1928).

is in agreement with experiment as first shown by Curie, and the characteristic temperature $\Theta^*$ is called *the Curie temperature.*

When $H_e$ is not zero, formula (6) leads to the following semi-quantitative results. At temperatures above the Curie temperature $\Theta^*$, as $H_e$ increases, $I$ increases from zero, and approaches the saturation value $I_\infty$ more rapidly than for a paramagnetic. For small values of $x$ we have

$$\tanh x \sim x. \qquad (1446,8)$$

Consequently for not too large $H_e$ and at sufficiently high $T$ formula (1) becomes approximately

$$\frac{I}{I_\infty} = \frac{\mu_0 H_e}{kT} + \frac{\Theta^*}{T}\frac{I}{I_\infty}, \qquad (1446,9)$$

or

$$\frac{I}{I_\infty} = \frac{\mu_0 H_e}{k(T-\Theta^*)}. \qquad (1446,10)$$

This relation is a particular example of the law

$$I/H_e \propto 1/(T-\Theta_W), \qquad (1446,11)$$

called Weiss' law. We have already mentioned in § 1415 that a relation of this form empirically represents the experimental data for rare earth ions at low temperatures, but only over a restricted range of temperatures. For ferromagnetics Weiss' law represents the experimental data over a rather wide range of temperatures, above and not too close to the Curie temperature. But the value of $\Theta_W$ which is found to fit is not quite equal to the Curie temperature. This discrepancy between theory and experiment is removed in the improved theory described in § 1448.

According to formula (9) at temperatures below $\Theta^*$ and not too near $\Theta^*$, the equilibrium value of $I$ is not much less than $I_\infty$ and is rather insensitive to $H_e$. This is in agreement with the experimental facts.

We shall not pursue Weiss' formulae any further in detail, because we shall be more concerned with more modern variations of the theory. Weiss' theory gives a good general account of ferromagnetics, provided we may choose $\Theta^*$ suitably. The Weiss coefficient which we have denoted by $k\Theta^*/\mu_0 I_\infty$ is about $10^4$, in contrast with the demagnetizing coefficient which is only $\frac{4}{3}\pi$. Weiss' theory depends on the *ad hoc* assumption of this large term proportional to $I$ in the energy of a single orientated magnet. Only after the development of quantum theory did it become possible to explain the origin of this important term in the energy.

**§ 1447. Quantal explanation of Weiss' field.** According to classical theory the origin of the high field proportional to $I$ postulated by Weiss remained a mystery. Its explanation by quantum theory was provided by

Heisenberg.* In metals we may safely assume that orbital angular momentum is quenched and we need consider only the orientation of spins. It is not within the scope of this book to give details of quantum theory, nor shall we do so here. We shall merely recall the explanation of molecule formation (covalency) first given by Heitler and London,† and state that there will be an interaction of a similar type between neighbouring atoms in a metal if each atom has a resultant spin. At least we can be sure that there will be a non-zero difference in the energy of the lowest quantum state, allowed by the requirement of antisymmetry in all electrons, according as each pair of neighbouring atoms have their spins parallel or antiparallel. To deduce the existence of ferromagnetism, one has to assume that the state of lower energy is that in which the spins are parallel. In the opposite case one would find at low temperatures a decrease and eventual disappearance of paramagnetism. This phenomenon is sometimes called antiferromagnetism but it has not yet been studied in detail,‡ and we shall not refer to it again. The conditions under which the energy difference between states of parallel and anti-parallel spin of neighbours has the right sign and is sufficiently large to produce ferromagnetism have as yet been only inadequately determined, and we shall not discuss them. We shall take it as a fact that the energy difference, which we know must always exist in fact, has the right sign and is sufficiently large in certain metals, notably iron, cobalt and nickel.

Having thus explained the origin of large terms in the energy of the assembly depending on the mutual orientations of atoms with electron spin, Heisenberg proceeded to develop a quantitative treatment of ferromagnetism. In this treatment the assembly is regarded as a cooperative assembly of magnetic atoms. The method of attack is rather similar to that described in Chapter XIII for the explanation of order-disorder in crystals, but the algebra is somewhat more complicated. In the first approximation the relation between $I$ and $H_e$ obtained for atoms in a doublet state ($S=\frac{1}{2}$) is precisely formula (1446, 6). The reader, who is interested, will find accounts of the method either in Heisenberg's papers or elsewhere.§ We shall instead describe an alternative and considerably simpler treatment due to Stoner, in which the atomic structure of the metal is ignored and the elementary magnets are assumed to be the electrons.

**§ 1448. Collective electron ferromagnetism.** In the detailed treatment of ferromagnetism Heisenberg's method of approach has proved in many ways less convenient than the alternative treatment of electrons in

* Heisenberg, *Zeit. Phys.* **49**, 619 (1928). † Heitler and London, *Zeit. Phys.* **44**, 455 (1927).

‡ See, however, Hulthen, *Proc. Sec. Sci. Amsterdam*, **39** (2), 190 (1936).

§ For example: Van Vleck, Chap. XII; Stoner, p. 358; *S.M.* pp. 485 *seq.*

metals already described in Chapter XI. The first approximation in this treatment is that of free electrons, for which the energy is purely kinetic, the number of states per unit energy range then being proportional to the square root of the energy. The effect of the periodic field of the lattice is to modify the distribution of states, giving rise to a series of energy bands, separate or overlapping. This model of a metal was first applied to ferromagnetism by Bloch,* and has been elaborated in great detail by Stoner, who calls the model *collective electron ferromagnetism*. The account which we give here is based entirely (and largely verbatim) on a paper by Stoner,† to which we refer the reader for all details.

Although elaborate calculation is necessary to determine the form of the electron bands with any precision, the energy density of states near the bottom of a band generally depends on the energy in the same way as for free electrons, but with a different proportionality factor; this holds also near the top of a band, the energy being measured downwards from that limit. The salient characteristics of metals depend on the electrons in unfilled bands. In particular, in the ferromagnetic metals, iron, cobalt and nickel, the ferromagnetism may be attributed to the electrons in the partially filled band corresponding roughly to the $d$-electron states in the free atoms. The exchange interaction is such that, at low temperatures, instead of the electrons occupying the lowest states in balanced pairs, there is an excess of electrons with spins pointing in one direction, giving rise to a spontaneous magnetization. The decrease of energy due to the exchange effect with increase in the number of excess parallel spins is accompanied by an increase due to the electrons moving to states of higher energy in the band. The equilibrium magnetization depends on the number of electrons, the form of the band, the magnitude of the exchange interaction, and the temperature, and must be calculated on the basis of Fermi-Dirac statistics. The purpose of the theory is the determination of the form of the magnetization-temperature curves for bands of the standard type and for a range of values of the exchange interaction energy.

With the assumption of a standard energy distribution of states in a band, precise calculations of the magnetization as a function of the temperature can be made. Owing to the peculiarities in the forms of the electronic energy bands of particular metals, it cannot be claimed that the results will necessarily be strictly applicable to any actual ferromagnetic. For the results to be applicable with fair approximation, however, it is merely necessary that the band form should approximate to the standard type over part of its range, up to and somewhat beyond the top of the Fermi distribution.

* Bloch, *Zeit. Phys.* 57, 545 (1929).
† Stoner, *Proc. Roy. Soc.* A, 165, 372 (1938), where references are given to earlier work.

As far as can be judged from the graphical representation of the form of the $d$-band in nickel (see Chapter XI, Fig. 4), the approximation is here reasonably close; the energy density of states near the top of the band (the portion here relevant) being roughly proportional to the square root of the energy measured downwards. It is difficult to say how far the general character of the results is likely to be affected by special peculiarities in the form of bands; but this question opens up such a wide range of possibilities that it is hardly profitable to pursue it, except with reference to more detailed information about the band form for a particular metal. The choice of the standard band form has the formal advantages that precise calculations are possible covering a wide range of variation of the relevant parameters, and that in the limit the results pass over into those obtained on the basis of classical statistics.

Following Stoner (with slight alteration of his notation) we use the following parameters: $\epsilon^*$ denotes the energy, measured from the bottom of the unfilled band, such that, in the absence of any external field and in the absence of exchange interaction, the number of states with energy less than $\epsilon^*$ is equal to the number of electrons. Alternatively, for an almost full band, $-\epsilon^*$ denotes the energy, measured from the top of the unfilled band, such that the number of states with energy greater than $-\epsilon^*$ is equal to the number of holes in the band (electrons needed to complete the band). $\Theta^*$ is a characteristic temperature, such that $k\Theta^*$ is a convenient measure of the exchange interaction energy. The more precise definition of $\Theta^*$ is given below, and is chosen such that in the classical limit $\epsilon^* \to 0$ the Curie temperature $T_c$, at which the spontaneous magnetization becomes zero, is equal to $\Theta^*$. The relative magnetization, denoted by $\xi$, is defined as the ratio of the number of excess parallel spins to the total number of potentially effective spins. Alternatively $\xi$ is the ratio of the intensity of magnetization $I$ to the saturation value $I_\infty$. The value of $\xi$ at $T = 0$ will be denoted by $\xi_0$. According to classical theory $\xi_0 = 1$, but we shall find that according to Fermi-Dirac statistics $\xi_0$ is not always unity.

We have still to define $\Theta^*$ more precisely. It can be shown that the effect of exchange interaction is to introduce into the energy a term proportional to the square of the magnetization. To an approximation analogous to that of Bragg and Williams in the theory of order-disorder (§ 1314), this is equivalent to assigning an energy term per electron of the form

$$\mp \alpha\beta I \quad (\alpha \text{ const.}), \tag{1448, 1}$$

where $\beta$ is Bohr's magneton and $\alpha$ a constant; the $-$ refers to electrons parallel, the $+$ to electrons antiparallel to $I$. We now define $\Theta^*$ by the formula

$$k\Theta^* = \frac{N}{V}\beta^2\alpha = I_\infty \beta\alpha. \tag{1448, 2}$$

Substituting for $\alpha$ from (2) into (1) we obtain for the energy term per electron due to exchange interaction

$$\mp k\Theta^* \frac{I}{I_\infty} = \mp k\Theta^* \xi. \qquad (1448, 3)$$

Thus $k\Theta^*$ is a measure of the exchange interaction energy such that $2k\Theta^*\xi$ is the change in total energy when the spin of a single electron is reversed. The difference in total energy per electron in the completely magnetized state ($\xi = 1$) and the unmagnetized state $\xi = 0$ is $\frac{1}{2}k\Theta^*$.

It is convenient to denote by $\epsilon$ the energy of any given state in the absence of an external field and in the absence of interaction. The complete form of the energy per electron in the presence of an external field $H_e$ is then

$$\epsilon \mp (k\Theta^*\xi + \beta H_e). \qquad (1448, 4)$$

If we denote the number of states of each spin in the range $\epsilon$ to $\epsilon + d\epsilon$ by $g(\epsilon)\,d\epsilon$, then for a band of the standard form containing $N$ electrons in all

$$g(\epsilon) = N\tfrac{3}{4}\epsilon^{\frac{1}{2}}/\epsilon^{*\frac{3}{2}}. \qquad (1448, 5)$$

In the presence of an external field or of exchange interaction we have to treat states of opposite spin separately. Using (4) we obtain for the grand partition function

$$\Xi = \int_0^\infty g(\epsilon)\log[1 + \lambda\exp\{-(\epsilon - k\Theta^*\xi - \beta H_e)/kT\}]\,d\epsilon$$
$$+ \int_0^\infty g(\epsilon)\log[1 + \lambda\exp\{-(\epsilon + k\Theta^*\xi + \beta H_e)/kT\}]\,d\epsilon. \qquad (1448, 6)$$

Substituting for $g(\epsilon)$ from (5) into (6), we obtain

$$\Xi = N\frac{3}{4}\left(\frac{kT}{\epsilon^*}\right)^{\frac{3}{2}}\int_0^\infty x^{\frac{1}{2}}\log[1 + \lambda\exp\{-x + (k\Theta^*\xi + \beta H_e)/kT\}]\,dx$$
$$+ N\frac{3}{4}\left(\frac{kT}{\epsilon^*}\right)^{\frac{3}{2}}\int_0^\infty x^{\frac{1}{2}}\log[1 + \lambda\exp\{-x - (k\Theta^*\xi + \beta H_e)/kT\}]\,dx. \qquad (1448, 7)$$

The value of $\lambda$ is determined, as usual, by

$$N = \frac{\partial\Xi}{\partial\log\lambda}, \qquad (1448, 8)$$

and the magnetization $IV$ by

$$IV = -kT\frac{\partial\Xi}{\partial H_e}, \qquad (1448, 9)$$

which can be written in the equivalent form

$$\xi = -\frac{kT}{N\beta}\frac{\partial\Xi}{\partial H_e}. \qquad (1448, 10)$$

We may note that, if we omit the exchange interaction terms $k\Theta^*\xi$ from (7), we recover formula (1439, 4) for a paramagnetic electron gas.

If one can eliminate $\lambda$ from (8) and (10) one can obtain $\xi$ as a function of $T$ and $H_e$. This has been done numerically by Stoner. We shall here only summarize the results very briefly, and we refer the reader to Stoner's paper† for all details.

We first recall the definition of a Curie temperature as the upper bound of the temperature region in which $\xi$ is not zero when $H_e = 0$. The calculation of $\xi$ as a function of $H_e$ above the Curie temperature $T_c$ is straightforward. The method of calculating the spontaneous magnetization below the Curie temperature is first to obtain values of $k\Theta^*/\epsilon^*$ corresponding to a series of values of $kT/\epsilon^*$ and of $\xi$. From these, values of $kT/\epsilon^*$ as a function of $\xi$ for a series of values of $k\Theta^*/\epsilon^*$ were obtained by inverse interpolation. The computational work was based largely on the use of accurate tabulated values of Fermi-Dirac functions prepared by McDougall and Stoner.‡

The character of the dependence of $\xi$ on $kT/\epsilon^*$ depends on the ratio $k\Theta^*/\epsilon^*$, the classical results of Weiss being obtained when $\epsilon^*/k\Theta^* \to 0$. A necessary condition for ferromagnetism is found to be

$$k\Theta^*/\epsilon^* > \tfrac{2}{3} \quad \text{(condition for ferromagnetism).} \qquad (1448, 11)$$

When $k\Theta^* = \frac{2}{3}\epsilon^*$ the Curie temperature is at the absolute zero. In the range of $\Theta^*$ defined by

$$2^{-\frac{1}{3}} = 0{\cdot}794 > k\Theta^*/\epsilon^* > \tfrac{2}{3}, \qquad (1448, 12)$$

as $k\Theta^*/\epsilon^*$ increases, the value $\xi_0$ of the relative magnetization at $T = 0$ increases steadily from 0 to 1. In the range

$$k\Theta^*/\epsilon^* > 2^{-\frac{1}{3}} = 0{\cdot}794 \qquad (1448, 13)$$

$\xi_0$ is unity. In particular in the classical limit, $\epsilon^* \to 0$, the value of $\xi_0$ is unity. Thus classically the saturation value of magnetization deduced from paramagnetism above the Curie temperature should be equal to the limiting value of the spontaneous magnetization at $T = 0$. Experimentally such an equality is not found. This difficulty of the classical theory is removed by the improved theory.

The results are conveniently summarized in diagrams. Fig. 14 shows the relative magnetization $\xi$ plotted against $kT/\epsilon^*$ for $T < T_c$, and the quantity $\beta H_e/\xi\epsilon^*$, proportional to the reciprocal of the susceptibility, plotted against $kT/\epsilon^*$ for $T > T_c$. Fig. 15 shows the same results plotted somewhat differently. The abscissa is here $T/T_c$; for $T > T_c$ the ordinate is $\xi_0\beta H_e/\xi kT_c$, proportional to the reciprocal of the susceptibility; for $T < T_c$ the ordinate is the spontaneous magnetization expressed as the fraction $\xi/\xi_0$ of its value at $T = 0$. It is to be noticed that these curves do not change monotonically with $k\Theta^*/\epsilon^*$ in the neighbourhood of $k\Theta^*/\epsilon^* = 0{\cdot}79$. As well as the numerical

† Stoner, *Proc. Roy. Soc.* A, **165**, 372 (1938).
‡ McDougall and Stoner, *Phil. Trans. Roy. Soc.* A, **237**, 67 (1938).

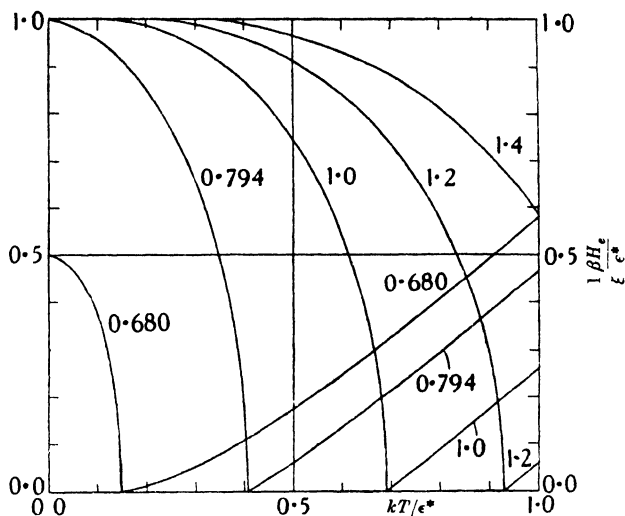



Fig 14 The falling curves (scale on left) give the spontaneous magnetization below the Curie point the rising curves (scale on right) a quantity proportional to the reciprocal of the susceptibility above the Curie point The numbers on the curves give the values of $k\Theta^*/\epsilon^*$

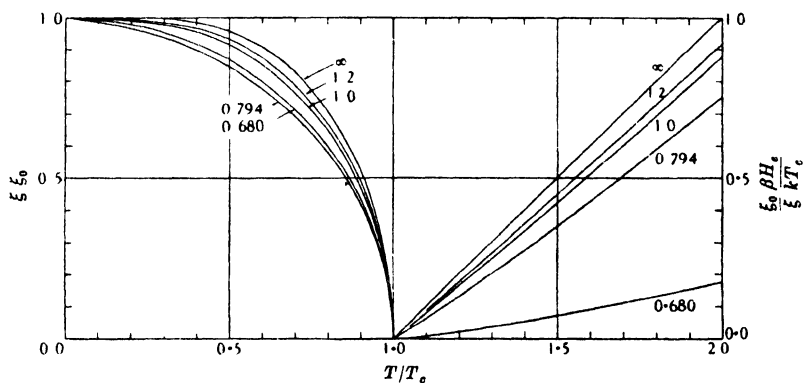



Fig 15 The falling curves (scale on left) give the reduced spontaneous magnetization below the Curie point, the rising curves (scale on right) a quantity proportional to the reciprocal of the susceptibility above the Curie point The numbers on the curves give the values of $k\Theta^*\ \epsilon^*$, the limiting curves labelled $\infty$ correspond to the use of classical statistics

results summarized in these diagrams, Stoner gives series expansions, appropriate for various ranges, for several relations, and in particular the relation between $k\Theta^*/\epsilon^*$ and $kT_c/\epsilon^*$.

In a later paper Stoner uses exactly the same methods to calculate the anomalous heat capacity due to the interaction between the spins, and in particular to calculate the discontinuity in this heat capacity at the Curie temperature. The reader is again referred to Stoner's paper† for details.

**§ 1449. Preliminary comparison with experiment.** In spite of the immense amount of experimental work on ferromagnetics, there are only extremely few data obtained under such conditions and with such materials as to avoid hysteresis. A systematic analysis of suitable data for comparison with the theory has been undertaken by Stoner, but he has as yet published only a discussion of the susceptibilities of iron ($\beta$- and $\delta$-phases), cobalt and nickel. The data of Sucksmith and Pearce are chosen by Stoner‡ as being more reliable than any previously obtained. For cobalt and nickel there is a closely linear relation between the reciprocal of the susceptibility and the temperature over a considerable temperature range. This was also found for vanadium alloys of iron containing sufficient vanadium (5 %) to suppress the $\gamma$-phase, which for pure iron extends from about 1190° K. to 1660° K.; the extrapolated slope for zero vanadium agreed closely with that obtained by joining the curves for pure iron in the $\beta$- and $\delta$-phases. Actually the experimental curves are not linear right down to the Curie point, the curves being convex towards the $T$-axis. Moreover, the temperature $\Theta_W$ occurring in the Weiss law

$$I/H_e \propto 1/(T-\Theta_W), \qquad (1449, 1)$$

valid over the straight portion, is considerably higher than the experimental Curie temperature $T_c$.

The experimental curve is, however, strikingly similar to the theoretical curves corresponding to Stoner's treatment described in the preceding section. The comparison is shown in Fig. 16, where the reciprocal of the reduced susceptibility is plotted against $T/T_c$. Theoretical curves are drawn for several values of $k\Theta^*/\epsilon^*$, including the curve (1) corresponding to the classical limit $\epsilon^* \to 0$; the curve (2) corresponds to the minimum value of $k\Theta^*/\epsilon^*$ for which $\xi_0 = 1$, that is to say for which the spontaneous magnetization at $T = 0$ is equal to the saturation magnetization. The experimental data for the three metals are all fitted by the same curve corresponding to a value of $k\Theta^*/\epsilon^*$ slightly less than $2^{-\frac{1}{3}}$, and to a value of $\xi_0$ between 1·0 and 0·9.

† Stoner, *Proc. Roy. Soc.* A, **169**, 339 (1939). ‡ Stoner, *Proc. Leeds Phil. Soc.* **3**, 457 (1938).

This preliminary test of Stoner's formulae is striking evidence of their usefulness, and it is to be hoped that other comparisons with experimental data may become available in the near future.

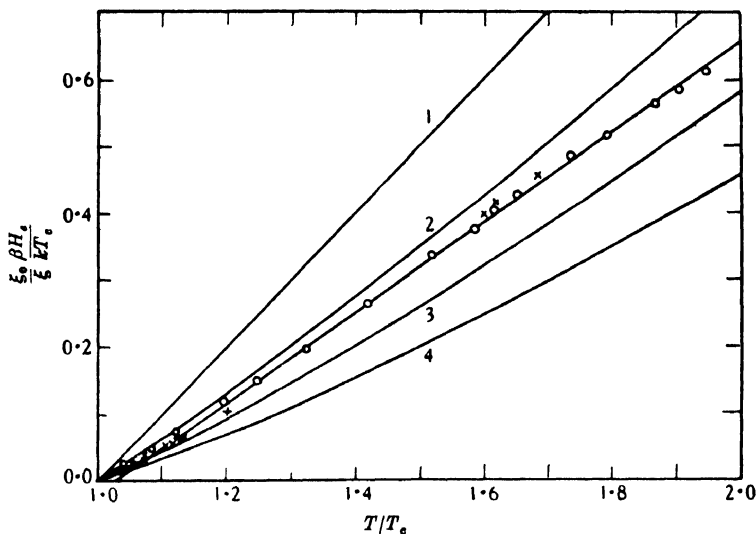



Fig. 16. Reciprocal of reduced susceptibility as a function of reduced temperature. Theoretical curves according to Stoner:

1. $k\Theta^*/\epsilon^* \to \infty$, $\xi_0 = 1{\cdot}0$.
2. $k\Theta^*/\epsilon^* = 0{\cdot}794$, $\xi_0 = 1{\cdot}0$.
3. $k\Theta^*/\epsilon^* = 0{\cdot}733$, $\xi_0 = 0{\cdot}9$.
4. $k\Theta^*/\epsilon^* = 0{\cdot}711$, $\xi_0 = 0{\cdot}8$.

Experimental points obtained by Sucksmith and Pearce:

○ Nickel. × Iron ($\beta$- and $\delta$-phases). + Cobalt.

# APPENDIX

*Note on p.* 131

§ A 1. Quite recently Kellermann* has determined rather accurately $g(\nu)$ for NaCl. A notable piece of theoretical work followed by prodigious calculations led to the evaluation of about 280 characteristic frequencies corresponding to about 6700 normal modes. From these he was able to obtain a good approximation to the distribution of all frequencies. The only experimental data used were the lattice constant and compressibility of the crystal. However a useful check was obtained in that for two other independent elastic constants of the crystal there was agreement between theory and experiment within the accuracy of the latter.

The form of $g(\nu)$ obtained by Kellermann is shown in Fig. A 1, which shows a strong resemblance to the distribution found by Blackman who, by using a much simpler model of the crystal, was able to determine the frequencies of as many as 30,000 normal modes. We refer below† to the use of the computed $g(\nu)$ to obtain the heat capacity of the crystal.

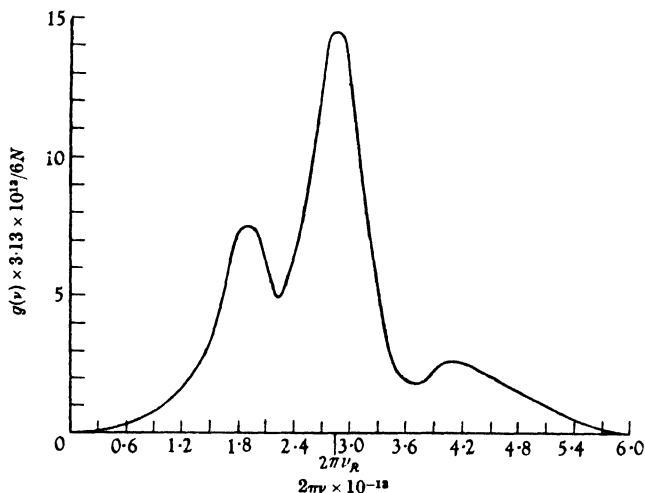



Fig. A 1. Frequency distribution of the sodium chloride crystal. $\nu_R$, frequency of residual rays.

* Kellermann, *Phil. Trans. Roy. Soc.* A, **238**, 513 (1940).

† See § A 2.

*Note on p. 147*

§ A 2. As mentioned above, Kellermann has computed $g(\nu)$ accurately for NaCl. From this $g(\nu)$ he has* then calculated $\Theta_D(T)$ as a function of $T$ and compared this with values obtained experimentally from the heat capacity. The result of this comparison is shown in Fig. A 2. The agreement could hardly be better.

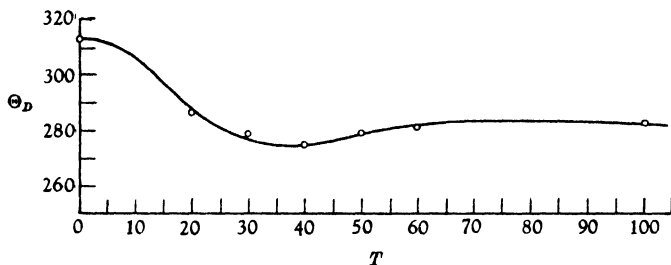



Fig. A 2. Temperature dependence of $\Theta_D$. The smooth line is drawn from experiments. ○, calculated values.

* Kellermann, *Proc. Roy. Soc.* A, **178**, 17 (1941).

*Note on p. 197*

§ A 3. The use of chemical constants is rapidly dying, their place being taken by numerical values of the thermodynamic functions $\mu$, $H$ and $S$. For this purpose the following table giving in numerical form contributions of several kinds of degrees of freedom may be found convenient.

TABLE A 1

| | $\frac{\mu}{kT} - \log_e \frac{p}{\text{atm.}}$ | $\frac{H}{kT}$ |
|---|---|---|
| Translation | $-7{\cdot}86 - \log_e M^{3/2}(T/100)^{5/2}$ | 2·50 |
| Rotation (linear molecules) | $-0{\cdot}92_5 - \log_e 10^{40} A(T/100)/\sigma$ | 1·00 |
| Rotation (non-linear molecules) | $-1{\cdot}96 - \log_e 10^{60}(ABC)^{1/2}(T/100)^{3/2}/\sigma$ | 1·50 |
| Each internal vibration | $-\log_e(1 - e^{-\Theta_v/T})$ | $\frac{\Theta_v/T}{e^{\Theta_v/T} - 1}$ |
| Residual energy | $E_0/kT$ | $E_0/kT$ |

In the table $M$ denotes the conventional 'molecular weight'. $A$, $B$, $C$ are moments of inertia measured in g.cm$^2$. $\sigma$ denotes the symmetry number. $\Theta_v$ is a characteristic temperature related to the frequency $\nu$ by $h\nu = k\Theta_v$. $E_0$ is a constant determined by the choice of zero of energy.

Corresponding expressions for the molecular entropy can be immediately derived from the identity

$$\frac{S}{k} = \frac{H}{kT} - \frac{\mu}{kT}.$$

*Note on p.* 202

§ A4. It is stated in the main text that neglect of the term in $T^{-1}$ in $\log r(T)$ will introduce an error into $i$. This statement is misleading, if not quite untrue. Its neglect will in fact* lead to assuming for $\chi$ a value differing slightly from its true value. Only if the true value of $\chi$ were known *a priori* would any discrepancy be apparent.

* We are indebted to Dr A. S. Coolidge for pointing this out.

*Note on p.* 286

§ A5. Quite recently Corner† has critically examined the experimental data for neon and argon. He comes to the conclusion that the experimental data on the density and energy of evaporation of the solid require a value of $m$ close to 12. He further finds that with $m = 12$ these experimental data together with those on the second virial coefficients of the gases are best fitted by the following values of the constants

Neon $m = 12$ $r^* = 3{\cdot}16\,\text{Å}$. $-\epsilon^* = 5{\cdot}01 \times 10^{-15}\,\text{erg}$.

Argon $m = 12$ $r^* = 3{\cdot}87\,\text{Å}$. $-\epsilon^* = 16{\cdot}5 \times 10^{-15}\,\text{erg}$.

The values for argon are very close to those previously chosen by Buckingham on the basis of the gas data alone.

† Corner, *Trans. Fara. Soc.* **44**, 914 (1948).

*Note on p.* 307

§ A6. The essential difference between reducible and irreducible clusters is wrongly described in the main text. A cluster is reducible if it consists of two parts connected by a single molecule. Thus ⊠⊔ is reducible to ⊠ and □.

*Note on p.* 347

§ A7. More extensive calculations have been carried out subsequently by Prigogine and Raulier.† Their results are given in Table A2, which includes values of $g_l$, $g_m$ defined by (809, 2), (809, 3) respectively as well as of $V/V^*$

† Prigogine and Raulier, *Physica*, **9**, 396 (1942).

and of $g$ defined by (808, 25). It should be emphasized that these sets of values satisfy the equation (811, 2). Since this equation itself is valid only provided $PV \ll kT$, it is only applicable at temperatures appreciably below the critical. We have accordingly included only the calculations for $\Lambda^*/kT > 10$. Assuming the correctness of these computations, we must regard Table A 2 as superseding Table 7 in the main text, and must suppose that Lennard-Jones and Devonshire's computations contained small numerical errors. In this case comparison between theory and experiment for all properties of the liquid may require some slight revision.

TABLE A 2

| $\frac{\Lambda^*}{kT}$ | $\frac{v}{v^*}$ | $g \times 10^4$ | $g_l \times 10^6$ | $g_m \times 10^6$ |
|---|---|---|---|---|
| 11·1 | 1·183 | 13·87 | 566 | 120 |
| 13·1 | 1·110 | — | — | — |
| 16 | 1·053 | 4·00 | 74 | 17 |
| 18 | 1·026 | 2·94 | 44·5 | 10·0 |
| 21 | 1·002 | 2·225 | 16·2 | 6·0 |
| 25 | 1·000 | 1·65 | 14·4 | 3·8 |
| 30 | 1·000 | 1·33 | 11 | 2·8 |

The relation (811, 11) between vapour pressure and temperature found by Lennard-Jones and Devonshire, namely

$$\log_e \frac{pV^*}{\Lambda^*} = 1{\cdot}92 - 0{\cdot}678\frac{\Lambda^*}{kT}, \qquad \text{(A 7, 1)}$$

according to Prigogine,† requires no modification. It is not made clear either in the main text or in the original paper that this formula does not represent at all accurately the real dependence of vapour pressure on temperature which is more like

$$\log_e \frac{pV^*}{\Lambda^*} = 0{\cdot}48 - 0{\cdot}544\frac{\Lambda^*}{kT}. \qquad \text{(A 7, 2)}$$

If we regard formulae (1) and (2) as describing graphs of log $p$ plotted against $T^{-1}$, both are straight lines. The two straight lines intersect at a point where $\Lambda^*/kT = 10{\cdot}7$. If we take the critical temperature $T_c$ to be given by $\Lambda^*/kT_c = 9$, we find that the intersection occurs at $T/T_c = 0{\cdot}84$. The boiling-point is at about $0{\cdot}6T_c$, which is near enough to the intersection for the discrepancy between the two formulae (1) and (2) to correspond to a difference of less than 10 % in $T$ for a given $p$. But for a given $T$ the discrepancy in $p$ is a factor of nearly 2.

† Prigogine, *J. de Physique*, **5**, 16 (1944).

*Note on p. 367*

§ A 8. Considerable progress has been made in the evaluation of combinatory factors of this kind.

Let $N_A$, $N_B$ denote the number of molecules of types $A$, $B$ respectively. Let each molecule $A$ occupy $r_A$ sites and each molecule $B$ occupy $r_B$ sites. The number of sites which are neighbours of any one site are as usual denoted by $z$. It will be assumed that the structure of both kinds of molecules are such that the elements which occupy a single site are interconnected in the molecule as a simple chain or a branched chain, but that there are no closed rings in the molecule. Parameters $q_A$, $q_B$ are defined by

$$z(r_A - q_A) = 2(r_A - 1), \quad \text{(A 8, 1)}$$

$$z(r_B - q_B) = 2(r_B - 1). \quad \text{(A 8, 2)}$$

The physical meaning of $q_A$ is that $zq_A$ is the number of sites neighbours of the $r_A$ sites occupied by a molecule $A$, excluding those neighbours of each site occupied by the next element of the same molecule. The physical meaning of $q_B$ is similar.

Let $\rho_A$ denote the number of distinct configurations of a molecule $A$ when one of its elements is fixed on a given site. $\rho_B$ is defined similarly. In the trivial case of molecules occupying a single site $\rho = 1$. For molecules occupying two sites $\rho = z/\sigma$ where $\sigma$ is the symmetry number of the molecule. For molecules occupying three sites there are three distinct cases. If the molecules are linear and rigid $\rho = z/\sigma$. If the molecules are non-linear and rigid $\rho = zz'/\sigma$ where $z'$ is the number of alternative sites for the third element when the first two elements have been placed. If the molecules are flexible $\rho = z(z-1)/\sigma$. For molecules occupying more than three sites there are numerous alternatives. The minimum value for $\rho$ is $z/\sigma$ for rigid straight molecules. The maximum value for $\rho$ is approximately $z(z-1)^{r-2}/\sigma$ for entirely flexible molecules, but this is slightly inaccurate because it includes certain configurations in which a long molecule bends back on itself and two elements occupy the same site; such configurations should of course be excluded, but the error due to their inclusion is probably small.

The number of distinguishable arrangements $g(N_A, N_B)$ of this assembly has been shown* to be

$$g(N_A, N_B) = \frac{(r_A N_A + r_B N_B)!}{N_A!\, N_B!} \left\{\frac{(q_A N_A + q_B N_B)!}{(r_A N_A + r_B N_B)!}\right\}^{\frac{1}{2}z} (\rho_A)^{N_A} (\rho_B)^{N_B}. \quad \text{(A 8, 3)}$$

* Guggenheim, *Proc. Roy. Soc.* A, **183**, 203 (1944).

From (3) we obtain for the partial vapour pressures of the species $A$ and $B$ respectively.

$$\frac{p_A}{p_A^0} = \frac{N_A}{N_A + r_B N_B/r_A} \left\{\frac{N_A + r_B N_B/r_A}{N_A + q_B N_B/q_A}\right\}^{\frac{1}{2}zq_A}, \tag{A 8, 4}$$

$$\frac{p_B}{p_B^0} = \frac{N_B}{N_B + r_A N_A/r_B} \left\{\frac{N_B + r_A N_A/r_B}{N_B + q_A N_A/q_B}\right\}^{\frac{1}{2}zq_B}. \tag{A 8, 5}$$

It is to be observed that, whenever $r_A = r_B$, from which $q_A = q_B$ follows automatically, formulae (4) and (5) reduce to Raoult's law.

We may mention the following special cases of $r_A \neq r_B$. The case $r_A = 2$, $r_B = 1$, is that discussed in § 821. As there mentioned, the formulae for $g(N_A, N_B)$ were first derived for this case by Chang.* Subsequently Miller† following a procedure similar to Chang derived the formulae for the case $r_A = 3$, $r_B = 1$. Furthermore through comparison of the formulae for $r_A = 2$, $r_B = 1$ with those for $r_A = 3$, $r_B = 1$. Miller by analogy correctly guessed the general formulae for $r_A =$ any value, $r_B = 1$. Although Miller gave no proof of these formulae this was an important step towards the solution by much simpler methods of the general case for any values of $r_A$, $r_B$.

Incidentally the extension of (3) to a mixture of more than two species presents no difficulty.

* Chang, *Proc. Roy. Soc.* A, **169**, 512 (1939); *Proc. Camb. Phil. Soc.* **35**, 265 (1939).

† Miller, *Proc. Camb. Phil. Soc.* **38**, 109 (1942); **39**, 54 (1943).

*Note on p.* 399

§ A 9. It should be noted that the functions $\sigma$ and $\tau$ are interrelated by

$$\tfrac{2}{3}\tau(x) + \tfrac{1}{3}\sigma(x) = \frac{1}{1+x}. \tag{A 9, 1}$$

*Note on p.* 597

§ A 10. In the main text the equivalence between Bethe's method (in the usual first approximation) and the quasi-chemical equations has been proved for assemblies of two kinds of molecules each occupying a single site. It can in fact be shown that for the most general mixture of several kinds of molecules each occupying any number of sites, Bethe's method always leads to the quasi-chemical equations of equilibrium. More precisely one would say that these quasi-chemical conditions are implicitly assumed in Bethe's method (in its usual first approximation). The proof, which is extremely simple, is as follows.*

* Guggenheim, *Proc. Roy. Soc.* A, **183**, 222 (1944).

In Bethe's method an approximate grand partition function is constructed for one (or two) central sites and their neighbours. There is one term in this grand partition function for each distinct manner of occupation of all the sites. Let $(A, A, S)$ denote the term in the grand partition function corresponding to a selected central site being occupied by an element of an $A$ molecule, a selected nearest neighbour being occupied by an element of a different $A$ molecule, and all the remaining sites central and neighbours being occupied in some specified manner denoted symbolically by $S$. Let $(B, B, S)$ be similarly defined. Let $(A, B, S)$ denote the term corresponding to the selected central site being occupied by an element of an $A$ molecule, the selected neighbour site by an element of a $B$ molecule, all the remaining sites, central and neighbours being occupied in the manner $S$. Let $(B, A, S)$ be defined similarly and correspond to the converse manner of occupation of the selected central and neighbour sites.

The essential approximation of Bethe's method is the assumption

$$\left.\begin{aligned}(A, A, S)/(A, B, S) \text{ independent of } S,\\ (B, A, S)/(B, B, S) \text{ independent of } S,\end{aligned}\right\} \tag{A 10, 1}$$

According to this assumption the two Bethe parameters $\epsilon$ and $\eta$ can be defined by

$$(A, A, S)/(A, B, S) = \epsilon/\eta, \tag{A 10, 2}$$

$$(B, A, S)/(B, B, S) = \epsilon\eta. \tag{A 10, 3}$$

It is usual to obtain further information concerning the relation between $\epsilon$ and $\eta$ by using the fact that the central site and its neighbour are physically equivalent. The following alternative procedure is simpler and at least as profitable.

Sum (2) and (3) over all $S$ obtaining

$$(A, A)/(A, B) = \epsilon/\eta, \tag{A 10, 4}$$

$$(B, A)/(B, B) = \epsilon\eta. \tag{A 10, 5}$$

where $(A, A)$ denotes the sum of all terms in the grand partition function corresponding to the selected central site being occupied by an element of an $A$ molecule and the selected neighbour site by an element of a different $A$ molecule; the $(A, B)$, $(B, A)$ and $(B, B)$ are similarly defined. Now divide (5) by (4) thus eliminating $\epsilon$ and obtaining

$$\frac{(A, B)(B, A)}{(A, A)(B, B)} = \eta^2. \tag{A 10, 6}$$

Since the central site and its neighbour are physically equivalent, it is obvious that

$$(A, B) = (B, A) \tag{A 10, 7}$$

and consequently (6) is equivalent to

$$\frac{\{(A,\ B)+(B,\ A)\}^2}{4(A,\ A)(B,\ B)} = \eta^2. \qquad \text{(A 10, 8)}$$

Now each term in the grand partition function is proportional to the frequency of occurrence of the manner of occupation to which that term refers. Moreover, there is no special significance attaching to the particular pair of sites selected as central site and its neighbour. The numbers of pairs of sites occupied both by elements of different $A$ molecules, both by elements of different $B$ molecules and one by an element of an $A$ molecule, the other by an element of a $B$ molecule are therefore proportional respectively to $(AA)$, $(BB)$ and $\{(A,\ B)+(B,\ A)\}$. Hence (8) is equivalent to the condition of quasi-chemical equilibrium, provided

$$\eta = e^{\ w\ zkT}, \qquad \text{(A 10, 9)}$$

which is precisely the values *assumed* for $\eta$ in Bethe's method.

To sum up, the two essential approximate assumptions of Bethe's method are (1) and (9). The two assumptions together lead immediately to the quasi-chemical conditions of equilibrium.

# INDEX

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